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FACTORS OF AVAILABILITY OF PLANT FOOD.

BY G. S. FRAPS.

Plant food which can be removed from the soil by a crop is said to be available. When fertilization with phosphoric acid produces a decided increase in crop, the soil is said to be deficient in available phosphoric acid. Deficiency in available potash or nitrogen is judged in the same way. A rich soil contains abundant supplies of available plant food; a poor soil may be deficient in one or more essential elements, though other influences may cause a soil which contains an abundance of available plant food to yield poor crops. The term "available" refers to the plant food which can be taken up from the soil by a crop and has especial reference to the effect of phosphoric acid, potash, or nitrogen in increasing yields.

Deficiency in available plant food is usually judged from plot or pot tests, with the use of different fertilizers. Field experiments must be carried out at least two years, and even then the conclusions are not always reliable.[2]

For several decades chemists have been endeavoring to devise a method for the determination of available plant food in soils. The search has been for solvents which would always

[1] This work was performed in this laboratory with the permission of Prof. W. A. Withers, Chemist.

[2] See Hartwell: Proc. Assoc. Offic. Agr. Chem., 1900, p. 73.

dissolve less phosphoric acid from soils deficient in this element than from fertile soils, and less potash from those deficient in potash than from fertile soils. While valuable results have been obtained in this work, we have as yet no method which can be relied upon to show whether a soil requires fertilization with potash or phosphoric acid. Solvents are known which furnish valuable data with certain kinds of soils, but fail with others. It is possible that this is in part due to the fact, as Hartwell[1] has pointed out, that the soils worked on may not be deficient in what they are supposed to be. It is also possibly due to lack of consideration of other factors than solubility.

Very often there is no relation between the plant food dissolved by a given method and the fertility of different soils. Under such circumstances, the rule has been to decide that the method of determining available plant food is at fault. The authors of a recent article, however, who assumed that the plant food dissolved by water from soils was a measure of the available food, have gone so far as to conclude that, since there is no relation between the water-soluble plant food in a soil and its fertility, the latter does not depend on the amount of available plant food in the soil, but on unknown physical factors.

Factors of Availability.

Considering availability as referring to the plant food taken from the soil by crops, under favorable conditions of moisture, temperature, etc., it is well to consider whether other factors than the solubility of the plant food are not involved. It is a very well-known fact that in the case of nitrogen the amount of nitrates is no measure of the available nitrogen, since the presence of 2 or 20 parts of nitrates per million is no indication how much or how little nitrates will be produced during the growing season of the crop. Further, complex silicates are known to decompose in the soil, with the production of more soluble compounds of potash. This process may take place so slowly as to be inappreciable from year to year, but in long

[1] See Hartwell: Proc. Assoc. Offic. Agr. Chem., 1900, p. 73.

periods of time weathering is of importance. Four factors, or rather groups of factors, may be considered as influencing to a greater or less extent the availability of any given element of plant food. These are as follows:

1. The quantity of the element present at the beginning of the growing season in forms of combination which can be directly absorbed by plants. This may be called *chemical availability*.

2. The condition of the soil particles. Compounds chemically available may be protected, or enclosed, so as not to be exposed to the action of soil moisture or plant roots. This may be called *physical availability*.

3. The amount of the element transformed during the growing season into forms of combination which can be directly absorbed by the plant. Processes of weathering slowly transform the less soluble into more soluble compounds. This factor is certainly of importance in the case of nitrogen; its importance in the case of potash and phosphoric acid remains to be determined. This factor may be called *weathering availability*.

4. The nature of the plant. Plants differ in their capacity for absorbing plant food. It has been disputed whether plants do not take up all their food from soil solutions, but however this may be, plants differ in their capacity to absorb food. We will call this factor *physiological availability*.

Thus four factors have been included under the term availability. Chemists have chiefly directed their attention to the first, namely, the chemical availability, more particularly with reference to the solubility of the plant food. The other factors cannot be disregarded until their non-importance has been established. It remains to be demonstrated whether the lack of success in finding a solvent for estimating available plant food is due to incomplete knowledge in regard to the soils worked on, or to neglect of those other factors, or both.

Chemical Availability.

The solvent power of plants has not yet been worked out. It is certain that plant roots can take up plant food dissolved

in the soil water, but to what extent they can act upon undissolved food is not known. The intimate contact of soil particles and roots, the presence of acid juices in the roots, and certain experiments, are in favor of the view that plants can take up food from other than the soil solution.

Cell walls of plant roots are semipermeable membranes, penetrable by K, PO_4 and other ions. On one side of the cell wall is an acid solution, which must be dissociated to a certain extent with the production of hydrogen ions; on the other side, the soil particles. According to the laws of diffusion, the hydrogen ions should penetrate the cell walls and act upon the soil particles, bringing insoluble bodies into solution.

Dietrich[1] grew plants in pots of new red sandstone and basalt, which was also allowed to weather in pots kept free from vegetation. At the end of the experiment the mineral matter in the plant was added to that dissolved from the soil by 1 per cent nitric acid, and the mineral matter made soluble by weathering was subtracted. The difference represents the solvent effect of the plants:

Solvent Action of Plants.

Plant.	Total mineral matter. Sandstone.	Basalt.
	Gram.	Gram.
Three lupine plants	0.6080	0.7492
Three pea plants	0.4804	0.7132
Eight wheat plants	0.0272	0.1958
Eight rye plants	0.0137	0.1316

This is certainly evidence that plants can take up mineral matter other than that in the soil solution. The figures also exhibit a striking difference in the solvent powers of the plants.

Physiological Availability.

A difference in the power of plants to take food from the soil has been recognized for some time. Kossovich[2] divides plants into five groups, according to their ability to assimilate the phosphoric acid of phosphates. 1. Plants of high capac-

[1] Jsb. Agr. Chem., 1863, p. 1.
[2] Expt. Sta. Rec., 13, 265.

ity—mustard, buckwheat, hemp, winter rye. 2. Plants of medium capacity—peas, barley, summer rye, beets. 3. Plants of low capacity—potatoes, vetch, oats. 4. Plants almost devoid of capacity—millet, flax, clover.

Wagner[1] states that under the most favorable conditions the following percentages of the nitrates added to a soil are recovered in the crop :

90 per cent by potatoes, carrots, turnips ;
75 per cent by oats and flax ;
60 per cent by barley, summer wheat, summer rye ;
55 per cent by rape, mustard.

Without going into the cause of these differences, it is clear that differences exist, and that a soil may contain sufficient available plant food for one crop, and yet be deficient in one or more elements for another.

Weathering Availability.

This is the term applied to the transformation of plant food from unavailable to chemically available forms during the growth of the crop. It is certainly of great importance in the case of nitrogen. The activity of weathering depends upon a number of sub-factors, such as the nature of the soil, the temperature, etc.

Reverse Weathering.—This term may be applied to chemical reactions in the soil which convert chemically available plant food into unavailable forms. Whether the fixing of potash salts by zeolitic silicates is not, in part, reverse weathering remains to be decided, but the transformation of soluble phosphates into aluminium and iron phosphates is very probably such a change.

EXPERIMENTAL PART.

Effect of Weathering upon Chemically Available Food.

The objects of this work were two : to ascertain if the effect of weathering upon chemically available potash and phosphoric acid could be neglected ; and second, to determine the

[1] Landw. Versuchs-Sta., 43, 137.

effect on weathering of various additions to the soil, particularly organic matter.

The plan of the experiment comprehended the use of several solvents to determine the effect of weathering. The work has, however, been confined to N/5 and N/50 nitric acid. The former solvent has been used to a considerable extent for the determination of available phosphoric acid and potash. While N/5 nitric acid cannot be asserted to be a measure of the chemically available plant food with soil, yet, since it has been used for available food, it will aid in deciding whether the factor of weathering is to be neglected. It is not believed by the author that the plant food dissolved by N/5 acid represents the chemically available plant food in the soil.

Plan of Experiment.—Three soils were selected, and from each soil a series of jars (containing 2500 grams soil) were prepared, with additions as follows:

Jars 1 and 11, nothing;
Jars 3 and 13, calcium carbonate (25 grams);
Jars 5 and 25, calcium sulphate (25 grams);
Jar 7, starch (200 grams);
Jar 9, sawdust (200 grams).

Jars 1, 3, 5, 7, and 9 were kept moist by the addition of water at the beginning of the experiment and at intervals during the period (three months). Jars 11, 13, and 15 were kept dry for comparison.

At the end of the period the samples were dried and potash and phosphoric acid determined with N/5 (and potash with N/50) nitric acid according to the methods of the Association of Official Agricultural Chemists for N/5 hydrochloric acid. The determinations were not made in duplicate.

The soils are described as follows:

1786. Sandy soil from the State farm of the North Carolina Department of Agriculture, furnished through Prof. B. W. Kilgore.

1787. Cecil sandy loam from farm of A. and M. College, near Raleigh. A good soil.

1788. Durham sandy loam from College farm. Very poor.

Weathering by Moisture.

The effect of moisture alone on chemically available potash and phosphoric acid (measured with N/5 nitric acid) is presented in Table I. Potash was determined by N/5 and N/50 acid, and the figures at the head of the columns refer to this fact. The difference between the moist soil with calcium carbonate and the dry soil with calcium carbonate does not represent the action of moisture alone, since the moisture brings the calcium carbonate into action. The same may be said with regard to the calcium sulphate.

There is an average increase of chemically available potash and phosphoric acid in two soils (about 10 per cent) and a decrease in one. A difference in the behavior of the three soils is to be observed. The general effect of moisture is to increase the chemically available plant food in the soils.

Calcium carbonate seems to decrease the effect of moisture, since a less gain or a greater loss of chemically available potash and phosphoric acid takes place in its presence.

Effect of Calcium Carbonate and Calcium Sulphate.

Table II. exhibits the effect of calcium carbonate and calcium sulphate. It is seen that their presence in the dry soil affects the amount of phosphoric acid or potash dissolved by N/5 or N/50 nitric acid. Either the presence of calcium salts affects the solvent power of nitric acid of this strength, or they act upon the soil during the extraction with the solvent. In any event, a soil containing 1 per cent calcium carbonate or sulphate would give up different quantities of chemically available plant food (measured by this solvent) than the same soil without the calcium salts, and the presence of these substances would have a profound effect upon the real or apparent chemical availability of plant food in the soil.

With calcium carbonate there is an average loss of chemically available phosphoric acid with two soils, and a loss of potash in every case. The loss is greatest with soil 1787 for N/5 acid, being about 30 per cent, and about the same with soil 1788 with N/50 acid. In every case, save one, moisture

Table I.—Effect of Moisture on Phosphoric Acid (P) and Potash (K).

Sample No.	Treatment.	Soil 1786.		Soil 1787.			Soil 1788.		
		P. Per cent.	K N/5. Per cent.	P. Per cent.	K N/5. Per cent.	K N/50. Per cent.	P. Per cent.	K N/5. Per cent.	K N/50. Per cent.
I	Moist	.....	0.0041	0.0070	0.0111	0.0054	0.0075	0.0080	0.0072
II	Dry	0.0047	0.0035	0.0077	0.0098	0.0061	0.0063	0.0090	0.0072
	Gain (+) or loss (—)		+0.0006	—0.0007	+0.0013	—0.0007	+0.0012	—0.0010	0.0000
3	Calcium carbonate (moist)	0.0034	0.0036	0.0078	0.0074	0.0035	0.0067	0.0068	0.0048
13	Calcium carbonate (dry)	0.0041	0.0033	0.0090	0.0073	0.0055	0.0066	0.0088	0.0045
	Gain (+) or loss (—)	—0.0007	+0.0003	—0.0012	+0.0001	—0.0020	+0.0001	—0.0020	+0.0003
5	Calcium sulphate (moist)	0.0061	0.0058	0.0114	0.0095	0.0039	0.0081	0.0061	0.0058
15	Calcium sulphate (dry)	0.0045	0.0032	0.0112	0.0080	0.0056	0.0073	0.0061	0.0057
	Gain (+) or loss (—)	+0.0016	+0.0026	—0.0002	+0.0015	—0.0017	+0.0008	0.0000	+0.0001
	Aver. gain (+) or loss (—)	+0.0005	+0.0012	—0.0007	+0.0010	—0.0015	+0.0007	—0.0010	+0.0001

Table II.—Effect of Calcium Sulphate and Carbonate on Phosphoric Acid (P) and Potash (K).

Sample No.	Treatment.	Soil 1786. P. Per cent.	Soil 1786. K N/5. Per cent.	Soil 1787. P. Per cent.	Soil 1787. K N/5. Per cent.	Soil 1787. K N/50. Per cent.	Soil 1788. P. Per cent.	Soil 1788. K N/5. Per cent..	Soil 1788. K N/50. Per cent.
13	Calcium carbonate (dry)	0.0041	0.0033	0.0090	0.0073	0.0055	0.0066	0.0088	0.0045
11	Dry	0.0047	0.0035	0.0077	0.0098	0.0061	0.0063	0.0090	0.0072
	Gain (+) or loss (—)	—0.0006	—0.0002	+0.0013	—0.0025	—0.0006	+0.0003	—0.0002	—0.0027
3	Calcium carbonate (moist)	0.0034	0.0036	0.0078	0.0074	0.0035	0.0067	0.0068	0.0048
1	Moist	0.0047[1]	0.0041	0.0070	0.0111	0.0054	0.0075	0.0080	0.0072
	Gain (+) or loss (—)	—0.0013	—0.0005	+0.0008	—0.0037	—0.0019	—0.0008	—0.0012	—0.0024
	Aver. gain (+) or loss (—)	—0.0010	—0.0004	+0.0011	—0.0031	—0.0013	—0.0003	—0.0007	—0.0026
15	Calcium sulphate (dry)	0.0045	0.0032	0.0112	0.0080	0.0056	0.0073	0.0061	0.0057
11	Dry	0.0047	0.0035	0.0077	0.0098	0.0061	0.0063	0.0090	0.0072
	Gain (+) or loss (—)	—0.0002	—0.0003	+0.0035	—0.0018	—0.0005	+0.0010	—0.0029	—0.0015
5	Calcium sulphate (moist)	0.0061	0.0058	0.0114	0.0095	0.0039	0.0081	0.0061	0.0058
1	Moist	0.0047[1]	0.0041	0.0070	0.0111	0.0054	0.0075	0.0080	0.0072
	Gain (+) or loss (—)	+0.0014	+0.0017	+0.0044	—0.0016	—0.0015	+0.0006	—0.0019	—0.0014
	Aver. gain (+) or loss (—)	+0.0006	+0.0007	+0.0040	—0.0017	—0.0010	+0.0008	—0.0024	—0.0015

[1] Dry.

increases the effect of the calcium carbonate in decreasing the amount of chemically available plant food present.

Calcium sulphate increases chemically available phosphoric acid in each soil; it decreases potash in two soils, and increases it in one.

The increase in phosphoric acid dissolved from soil 1787 is very striking, being over 35 per cent. The solution was darker from the presence of more dissolved iron.

The decrease in dissolved potash is 15 to 25 per cent. The effect of calcium salts seems certainly to decrease the real or apparent chemically available potash as measured by N/5 or N/50 nitric acid, as a rule, the exception being soil 1786, in which the increase (moist) was about 40 per cent. This statement seems to be in conflict with the general opinion that calcium salts liberate potash; however, this liberation refers to aqueous solution, and does not refer to nitric acid solution, so that the conflict is not real.

Effect of Decaying Vegetable Matter.

These samples were provided with sawdust or starch and kept moist so as to allow decomposition. Two corrections were made in the results; first they were calculated to a soil containing the original amount of ignition residue, thus eliminating the effect of varying quantities of organic matter, and second, the potash in the starch or sawdust was subtracted. This correction was certainly too high in the case of the sawdust, as not half of it had decayed, but nevertheless, the results show plainly the effect of the organic matter.

The results are presented in Table III. First is to be noted an average loss of chemically available phosphoric acid (measured by N/5 nitric acid). Possibly the phosphoric acid enters into combination with the humus.

Next will be observed a very decided increase in chemically available potash. The increase is greatest with the poor soil, 1788, being nearly 100 per cent; with soil 1787 the increase is about 35 per cent. These figures show that considerable changes may take place in chemically available potash in the presence

Table III.—Effect of Organic Matter on Phosphoric Acid (P) and Potash (K).

Sample No.	Treatment.	Soil 1786.		Soil 1787.			Soil 1708.		
		P. Per cent.	K N/5. Per cent.	P. Per cent.	K N/5. Per cent.	K N/50. Per cent.	P. Per cent.	K N/5. Per cent.	K N/50. Per cent
7	Starch (moist)	0.0039	0.0053	0.0059	0.0154	0.0076	0.0060	0.0153	0.0084
1	Moist	0.0047[1]	0.0041	0.0070	0.0111	0.0054	0.0075	0.0080	0.0072
	Gain (+) or loss (—)	—0.0008	+0.0012	—0.0011	+0.0043	+0.0022	—0.0015	+0.0073	+0.0012
4	Sawdust (moist)	0.0041	0.0044	0.0072	0.0146	0.0057	0.0053	0.0165	0.0076
1	Moist	0.0047[1]	0.0041	0.0070	0.0111	0.0054	0.0075	0.0080	0.0072
	Gain (+) or loss (—)	—0.0006	+0.0003	+0.0002	+0.0035	+0.0003	—0.0022	+0.0085	+0.0004
	Aver. gain (+) or loss (—)	—0.0007	+0.0007	—0.0007	+0.0039	+0.0012	—0.0019	+0.0079	+0.0008

[1] Dry.

of organic matter. The decaying organic bodies act upon the soil, changing unavailable potash into available forms. The effect of stable manure would be to liberate potash, as well as to furnish plant food and change the physical properties of the soil. This may be a very important function of vegetable matter in the soil.

The presence of vegetable matter in a soil would have a decided effect on the chemically available plant food present at the beginning and at the end of the growing season.

Summary and Conclusions.

1. Availability of plant food, as measured by plant tests, includes four factors: chemical availability, physical availability, physiological availability, and weathering availability.

2. Chemically available plant food is that present in forms that can be taken up directly by plants.

3. Physical availability refers to enclosure in soil particles or protection of chemically available food.

4. Physiological availability refers to the difference in power of plants to assimilate food.

5. Weathering availability refers to the conversion of plant food into chemically available forms during the growing season of the plant.

6. The effect of weathering under different conditions was studied on three soils, the chemical available plant food being measured by N/5 or N/50 nitric acid. The results vary somewhat with the nature of the soil.

7. Moisture alone causes an average increase in chemically available potash and phosphoric acid in the soils. The increase is not large.

8. Calcium sulphate and calcium carbonate cause an average decrease in chemically available potash. Calcium carbonate causes a decrease in phosphoric acid, calcium sulphate an increase, which is especially large in one case.

9. The presence of calcium salts in a soil has a decided influence on the potash and phosphoric acid extracted by N/5 nitric acid.

10. Starch or sawdust, in decaying, decreases the chemically available phosphoric acid but in each case increases the potash, as much as 100 per cent in one case.

11. Stable manure is valuable not only for the plant food in it, but for its action in liberating potash.

12. Weathering availability cannot be entirely disregarded in considering available phosphoric acid and potash in soils, particularly when calcium sulphate or carbonate or much organic matter is present in the soil.

This investigation will be continued.

Contribution from the Kent Chemical Laboratory of the University of Chicago.

THE MOLECULAR REARRANGEMENT OF AMINOPHENYLALKYL CARBONATES.

By Henry T. Upson.

PART III.[1]

The only derivative of this class of compounds that was known when this work was undertaken was aminophenylethyl carbonate, which was obtained by Ransom by the reduction of *o*-nitrophenyl ethyl carbonate. The latter, in turn, was readily obtained by the treatment of *o*-nitrophenol in alkaline solution with ethyl chlorformate. In preparing new compounds of the above class, the same general method was followed, varying the nature of the nitrophenol from which a start was made. The purification of the derivatives is a matter of considerable difficulty, and particular care was therefore bestowed on preparing the nitrophenols in a perfectly pure condition. In many cases long and complex processes of separation of isomeric nitro compounds were repeatedly used, to insure purity. Besides this precaution, it was found that the successful reduction of each nitrophenyl alkyl carbonate to the amine required a special study of the particular conditions under which a good yield of the amine could be obtained. In view of the instability of these amines, their liability to rearrangement and to saponification, such a result was not unexpected. In the following description of the com-

[1] For Parts I. and II., *vide* Stieglitz and Upson: This Journal, 31, 458 (1904).

pounds prepared, attention will therefore be paid particularly to the experimental details of this part of the method of preparation. The experience gained with rather a large number of such compounds made it possible, finally, to isolate 4-chlor-2-aminophenyl acetate (see Part IV.) as the first *o*-aminophenyl ester of an acid other than carbonic acid. Böttcher had been unable to isolate such an amine as an intermediate product in the reduction of *o*-nitrophenyl benzoate, and in this laboratory all previous attempts at the preparation of such a body had proved unsuccessful.

EXPERIMENTAL PART.

p-Nitrophenyl Methyl Carbonate was obtained by the action of methyl chlorformate on *p*-nitrophenol in alkaline solution. It is a white solid soluble in ether and alcohol (m. p. 111° to 112°). It was not analyzed but was identified by the reduction to the

Hydrochloride of p-Aminophenyl Methyl Carbonate, $CH_3O_2\overset{1}{C}OC_6H_4\overset{4}{N}H_2.Cl$.—This was prepared by treating the *p*-nitro carbonate with stannous chloride and hydrochloric acid. There was some difficulty in getting the body pure; although after reduction a large yield of the white body was obtained by Ransom's method,[1] the substance invariably turned silver nitrate black, and figures obtained from different analyses did not agree. Enough of the pure hydrochloride to make the conductivity measurements was obtained as follows:

The white solid obtained by reducing the nitro body with stannous chloride was added slowly to potassium hydroxide which had been ground to powder and covered with 50 cc. of absolute ether, to which 1 cc. of water had first been added. The impure hydrochloride was stirred thoroughly through the potassium hydroxide, the ether decanted and dried, and hydrogen chloride passed in. The white precipitate which formed was the pure hydrochloride, as is shown by the analysis.

For this, and the other hydrochlorides which will be de-

[1] This JOURNAL, 23, 48 (1900).

scribed, the analyses were made by titration with N/10 silver nitrate solution, potassium chromate being used as indicator. The solutions were first neutralized with sodium carbonate.

0.2111 gram substance required 10.39 cc. N/10 $AgNO_3$.

	Calculated for $C_8H_{10}O_2NCl$.	Found.
Cl	17.41	17.44

The body showed no tendency to rearrange when left in water for many hours.

o-Nitrophenyl methyl carbonate obtained from *o*-nitrophenol and methyl chlorformate is a yellow mobile oil.

Hydrochloride of o-Aminophenyl Methyl Carbonate, $CH_3O_2\overset{1}{C}O\overset{2}{C_6}H_4NH_2Cl$, was prepared by reducing the oil with tin and hydrochloric acid in the cold.[1] The mixture was added to concentrated cold alkali, extracted with ether, and the extract precipitated with dry hydrogen chloride. The yield of the pure white solid was 80 per cent.

0.2562 gram substance required 12.56 cc. N/10 $AgNO_3$.

	Calculated for $C_8H_{10}O_2NCl$.	Found.
Cl	17.41	17.38

The tendency of this body to rearrange and the conclusions drawn from the conductivity measurements have been discussed in a previous paper.[2]

A large yield of *o*-nitro-*p*-cresol was obtained by nitrating *p*-toluidine, diazotizing the crude amine, and distilling the product with steam. The yield of the pure nitrocresol, melting at 34° C., was between 75 and 80 per cent. This method was found better and a larger yield was obtained than by the direct nitration of *p*-cresol.[3]

2-Nitro-4-methylphenyl Ethyl Carbonate, $\overset{2}{NO_2}\overset{4}{CH_3}C_6H_3.\overset{1}{O}CO_2C_2H_5$.—The addition of ethyl chlorformate to the alkaline solution of the nitrocresol should be slow and the mixture shaken. A yellow oil forms which solidifies on cooling. After crystallization out of alcohol it melts at 56°.

[1] This JOURNAL, **23**, 43 (1900).
[2] Stieglitz and Upson: *Ibid.*, **31**, 458 (1904).
[3] Brasch and Freyss: Ber. d. chem. Ges., **24**, 1960 (1891).

0.1904 gram substance gave 0.3696 gram CO_2 and 0.0844 gram H_2O.

	Calculated for $C_{10}H_{11}O_3N$.	Found.
C	53.33	52.93
H	4.89	4.93

3-Methyl-6-oxyphenylurethane, $\overset{3}{C}H_3(\overset{6}{O}H)C_6H_3.\overset{1}{N}HCO_2C_2H_5$. —Ten grams of 2-nitro-4-methylphenyl ethyl carbonate were dissolved in alcohol, 25 cc. concentrated alcohol added, and then slowly 12 grams granulated tin. After standing an hour the solution was filtered and an equal volume of water added. The mixture was allowed to stand over night and the following morning a quantity of white needles had formed. These were soluble in alkali, insoluble in acid, and melted after crystallization from alcohol at 101° C. The crystals continued to form slowly for several days.

A more rapid method for the preparation is as follows: Ten grams of the *o*-nitro-*p*-methylphenyl ethyl carbonate were placed in a flask with 24 cc. concentrated hydrochloric acid and 14 grams of powdered tin added slowly, the vessel being kept cold. Towards the end of the reduction the solution was allowed to come to ordinary temperature. As soon as the solution became clear it was filtered through glass wool, and after the addition of an equal volume of water, was heated to boiling for a few minutes. On cooling, a solid separated which, recrystallized from alcohol, melted at 101°. If care was not taken to avoid heat during the reduction, a body was invariably obtained which melted constantly at 77°, and an analysis did not give figures corresponding to any possible constitution, nor could it be proved to be a mixture by fractional crystallization. It was afterwards found, however, to be a mixture of carbonylaminocresol (m. p. 128°), and the urethane melting at 101°. These two bodies mixed in equal quantities melt at 77°.

0.1408 gram substance gave 0.3172 gram CO_2 and 0.0855 gram H_2O.

	Calculated for $C_{10}H_{13}O_3N$.	Found.
C	61.53	61.45
H	6.66	6.74

To fully establish the constitution of the urethane melting at 101° it was prepared from the hydrochloride of *o*-amino-cresol and ethyl chlorformate. One gram of the salt was suspended in absolute ether and a slight excess of sodium carbonate, dissolved in a little water, was added. After being shaken with the ethereal solution, which had now become slightly brown, the water was separated and 0.5 molecule of ethyl chlorformate added slowly. After filtration and evaporation of the ether a solid remained which, without recrystallization, melted at 101°. Mixed with the urethane prepared by the rearrangement method there was no depression of the melting-point. The properties of this body in other respects were identical with those of the rearranged body formed by the reduction of the nitrocresyl carbonate.

Carbonyl-o-amino-p-cresol, $\overset{1}{O}\underset{\llcorner\!\!\!

0.1539 gram substance gave 13.5 cc. N. at 26°.5 and 753 mm.

	Calculated for $C_{10}H_7O_2N$.	Found.
N	9.39	9.60

The Hydrochloride of 2-Amino-4-methylphenyl Ethyl Carbonate, $C_2H_5O_2\overset{1}{C}O\overset{4}{C}_6H_3\overset{2}{C}H_3NH_2Cl$.—In the first attempt to reduce the 2-nitro-4-methylphenyl ethyl carbonate, an alcoholic solution of the nitrocarbonate was used. This was done because, at the low temperature at which the experiment was to be carried out, the reduction was very slow. Previous experiment had shown that the amine would quickly suffer rearrangement, and it was important to have the reduction completed as soon as possible. The attempts, however, to isolate the amine hydrochloride after reduction in alcoholic solution were unsuccessful, because, as was afterwards found out, the amine hydrochloride is quite soluble in ether containing alcohol, and could therefore not be precipitated from the ethereal solution by the method which we used.

The following method gave a yield of 70 per cent of the pure amine hydrochloride. Two grams of the nitro compound were covered with 15 cc. of concentrated hydrochloric acid and cooled to about 10°. More than the calculated amount of granulated tin was added in small portions, the vessel being constantly shaken and the nitrocarbonate kept as finely divided as possible by rubbing with a glass rod. The temperature was not allowed to rise above the temperature of the hand. If the reduction is slow, the entire vessel will fill with a white mass which contains both organic and inorganic matter and is probably a tin double salt. If filtration is made after the reduction has been going on but for a short time, the precipitation of the tin double salt may be avoided. The best results, however, were obtained by allowing the reduction to continue until all of the nitrocarbonate had disappeared. The contents of the vessel were then cooled and added slowly to a very cold solution of 50 grams potassium hydroxide dissolved in 50 cc. of water. The mixture was extracted a number of times with absolute ether

and dried with solid potassium hydroxide. Into the filtrate a slow stream of dry hydrogen chloride was passed, and a copious white precipitate was formed. This was filtered and dried at once on a clay plate in a desiccator. It is soluble in alcohol and dilute acid, and melts with decomposition at 135° to 137°.

0.1545 gram hydrochloride required 6.75 cc. N/10 $AgNO_3$.

	Calculated for $C_{10}H_{14}O_3NCl$.	Found.
Cl	15.34	15.44

The reduction was also carried out with concentrated hydrochloric acid and zinc dust. The result was in general the same as that obtained with granulated tin.

One-half gram of the hydrochloride was dissolved in as little water as possible and a concentrated solution of chlorplatinic acid added. In a few minutes the chlorplatinate formed as a yellow precipitate. This was filtered and washed with ether containing a little alcohol. The chlorplatinate is insoluble in ether, but soluble in alcohol. It melted above 171°, with blackening.

0.0140 gram substance gave 0.0034 gram Pt.

	Calculated for $C_{20}H_{30}O_6N_2PtCl_6$.	Found.
Pt	24.28	24.28

3-Methyl-6-oxyphenylurethane, $CH_3^3(OH)^6C_6H_3^1NHCO_2C_2H_5$.—One gram of the hydrochloride was dissolved in water and in a very short time white needles separated from the solution. These continued to form for more than twenty-four hours. The crystals melted at 101°, and, mixed with the urethane prepared as above, showed no depression of the melting-point. Other properties were also identical. This is in fact the best and quickest method for obtaining perfectly pure 3-methyl-6-oxyphenylurethane.

2-Nitro-m-cresol (m. p. 56°) was prepared by nitrating *m*-cresol in glacial acetic acid solution at a low temperature with fuming nitric acid and distilling the product with steam.[1]

[1] Staedel and Kolb: Ann. Chem. (Liebig), 259, 210 (1890).

2-Nitro-5-methylphenyl Ethyl Carbonate.—From an alkaline solution of the nitrocresol (m. p. 56°) and ethyl chlorformate a yellow oil separated which solidified when the vessel was cooled to —5°, but remained an oil at ordinary temperatures. Allowed to stand with a solution of potassium hydroxide it becomes red, showing a gradual saponification to the potassium salt of *o*-nitro-*m*-cresol.

0.3030 gram substance gave 17.55 cc. N at 25° and 730 mm.

	Calculated for $C_{10}H_{11}O_4N$.	Found.
N	6.22	6.24

Hydrochloride of 2-Amino-5-methylphenyl Ethyl Carbonate, $C_2H_5O_2\overset{1}{C}O\overset{5}{C_6}H_3\overset{2}{C}H_3NH_2Cl$.—Two grams of the carbonate were reduced by the method described above for the isomeric compound and the hydrochloride of the amine was isolated in the same way. The yield was 60 to 70 per cent.

0.1695 gram substance required 7.35 cc. of N/10 $AgNO_3$.

	Calculated for $C_{10}H_{14}O_2NCl$.	Found.
Cl	15.34	15.37

The hydrochloride (0.4 gram) was dissolved in a very little water and a concentrated solution of chlorplatinic acid was added. A yellow precipitate formed which was filtered and washed with ether containing a little alcohol.

0.0210 gram chlorplatinate gave 0.0051 gram Pt.

	Calculated for $C_{20}H_{30}O_4N_2PtCl_6$.	Found.
Pt	24.28	24.27

4-Methyl-6-oxyphenylurethane, $\overset{4}{C}H_3(\overset{6}{O}H)C_6H_3\overset{1}{N}HCO_2C_2H_5$.—One gram of the hydrochloride of the amine was treated with water. The entire solid went into solution at once, but on standing crystals began to form and continued to form for several hours. The crystals were soluble in alcohol, ether, and chloroform, insoluble in acid, but soluble in alkali. They melted, after recrystallization from boiling water, at 95°.

0.1295 gram substance gave 0.2915 gram CO_2 and 0.0781 gram H_2O.

	Calculated for $C_{10}H_{13}O_4N$.	Found.
C	61.53	61.39
H	6.66	6.71

2-Nitro-6-methylphenyl ethyl carbonate was obtained from *o*-nitro-*o*-cresol[1] (m. p. 70°) as a yellow oil. This was extracted with ether which was allowed to evaporate and, on cooling, the oil crystallized to yellow needles. For purification they were dissolved in alcohol and precipitated by water. 2-Nitro-6-methylphenyl ethyl carbonate readily remains an oil at ordinary temperatures, but the pure crystals showed a melting-point of 32° to 33°. A slight impurity prevents solidification to a great extent. Five grams of the oil were kept in cold winter weather for more than a week below 0° without solidifying. The first combustion gave figures which were high for nitrogen, but after two crystallizations from alcohol a pure body was obtained.

0.3554 gram substance gave 21.5 cc. N at 24° and 724 mm.

	Calculated for $C_{10}H_{11}O_4N$.	Found.
N	6.22	6.50

Hydrochloride of 2-Amino-6-methylphenyl Ethyl Carbonate, $C_2H_5O_2\overset{1}{C}O\overset{6}{C_6}H_3\overset{2}{C}H_3NH_2Cl$.—Considerable difficulty was experienced in reducing 6-methyl-2-nitrophenyl ethyl carbonate. This may have been due to the quality of tin which was used at this stage of the experiment,[2] or to a failure to find the proper temperature at which the reduction could be carried out. The final method, which gave about 65 to 70 per cent yield of the amine hydrochloride was as follows:

One gram of the carbonate (m. p. 32°) was covered with 12 cc. concentrated hydrochloric acid and cooled. An excess of granulated tin was added and the whole shaken and kept cold. (A reduction was afterwards carried out at ordinary temperature with a good result except a slight brown appear-

[1] A. W. Hofmann and Miller: Ber. d. chem. Ges., **14**, 561 (1881); R. Hirsch: *Ibid.*, **18**, 1512 (1885).

[2] The quality of the tin used had quite an influence upon the result of the reductions carried out in this work. Recourse has been had to three separate shipments of granulated tin. The last, which was obtained from Kahlbaum, gave much the best results.

ance of the final product.) After a time the vessel filled with a white solid which was added slowly to a very cold solution of potassium hydroxide (1 : 1). The dried ethereal extract gave with dry hydrogen chloride the salt as a white precipitate. A little alcohol in the ether or the presence of traces of water diminishes the yield. The hydrochloride is very soluble in water, soluble in alcohol, but insoluble in ether.

0.2022 gram substance required 8.84 cc. N/10 $AgNO_3$.

	Calculated for $C_{10}H_{14}O_2NCl$.	Found.
Cl	15.34	15.49

A saturated solution of chlorplatinic acid was added to a saturated solution of the hydrochloride. A yellow precipitate formed which, after being washed with ether containing a little alcohol and dried in a vacuum-desiccator, was analyzed.

0.351 gram substance gave 0.0850 gram Pt.

	Calculated for $C_{20}H_{32}O_4N_2PtCl_6$.	Found.
Pt	24.28	24.22

5-Methyl-6-oxyphenylurethane, $CH_3^5(OH)^6C_6H_3^1NHCO_2C_2H_5$. —One gram of the hydrochloride of the amine dissolved in water gradually gave white needles on standing. These were soluble in alcohol and ether, insoluble in acid, but soluble in alkali. They melted after crystallization from hot water at 74° to 76°.

0.2051 gram substance gave 0.4610 gram CO_2 and 0.1255 gram H_2O.

	Calculated for $C_{10}H_{13}O_3N$.	Found.
C	61.53	61.31
H	6.66	6.80

The 4-chlor-2-nitrophenol used for the following experiments was prepared both by the nitration of the crude product obtained by the chlorination of phenol according to the method of Faust and Saame,[1] and also by nitration of pure *p*-chlorphenol. In both cases the body melting at 87° was obtained, but it was found, owing to the impurities in the crude

[1] Ann. Chem. (Liebig), Suppl., 7, 191 (1870).

product, that we could save time by first preparing the pure chlorphenol and nitrating afterwards.

4-Chlor-2-nitrophenyl Ethyl Carbonate.—Ten grams 4-chlor-2-nitrophenol were dissolved in a slight excess of potassium hydroxide solution and heated until all was in solution. A little more than 1 molecule of ethyl chlorformate was added slowly, with shaking. A light-yellow oil formed, which crystallized on cooling. It was filtered and washed with dilute potassium hydroxide solution, afterwards with water, and finally crystallized out of hot alcohol. An almost white solid was obtained, which melted at 60°.

0.3421 gram substance gave 18 cc. N at 21° and 745 mm.

	Calculated for $C_9H_8O_4NCl$.	Found.
N	5.72	5.91

The Hydrochloride of 4-Chlor-2-aminophenyl Ethyl Carbonate, $C_2H_5O_2\overset{1}{C}O\overset{4}{C}lC_6H_3\overset{2}{N}H_3Cl$.—In the first effort to reduce the carbonate with tin and hydrochloric acid in the cold, it was found that the reduction was very slow and the final product impure. The reduction could, however, be carried out much more rapidly at ordinary temperature, and the following method gave a 70 per cent yield of the pure product:

Three grams of carbonate were covered with 15 cc. of concentrated hydrochloric acid and cooled to about 10°. More than the calculated amount of granulated tin was added in small quantities and the vessel shaken, care being taken not to allow too much heat to generate. The solution cleared up somewhat, but after more than an hour the vessel filled with a white solid. This white body was added slowly with shaking to a very cold solution of 50 grams potassium hydroxide in 50 cc. water. The ethereal extract, treated in the same way as in previous cases, gave the hydrochloride as a white precipitate clinging somewhat to the sides of the vessel. It was filtered and dried on a clay plate in a desiccator. The body is fairly soluble in concentrated hydrochloric acid and glacial acetic acid, but insoluble in water and in alkali. It is soluble in alcohol, insoluble in benzene and chloroform. For

analysis the solid was covered with water, the mixture carefully heated to about 75°, and after being cooled titrated with silver nitrate solution, potassium chromate being used as indicator.

0.1467 gram substance required 5.85 cc. N/10 $AgNO_3$.

	Calculated for $C_8H_{11}O_2NCl_2$.	Found.
Cl	14.06	14.13

Two parts of the hydrochloride were dissolved in as little absolute alcohol as possible, and 1 part of a concentrated absolute alcohol solution of chlorplatinic acid added. The mixture was rubbed and stirred for a short time, and then an excess of absolute ether was added. An almost quantitative yield of yellow needles was precipitated. They decomposed somewhat at about 140°, and softened at 175° to 180°.

0.0675 gram chlorplatinate gave 0.0157 gram Pt.

	Calculated for $C_{16}H_{20}O_4N_2PtCl_6$.	Found.
Pt	23.17	23.30

A remarkable property of the hydrochloride of 4-chlor-2-aminophenyl ethyl carbonate, compared with the bodies of the series described above, is its insolubility in water. The other hydrochlorides dissolve instantly in water at 0°. The hydrochloride of *p*-chlor-*o*-aminophenyl ethyl carbonate, covered with water at 25°, showed practically no tendency to dissolve, and only when heated to 92° did it go into solution, and then, no doubt, only because it had been rearranged.

3-Chlor-6-oxyphenylurethane, $^{3}Cl(^{6}OH)C_6H_3{}^{1}NHCO_2C_2H_5$. — One gram of the hydrochloride was covered with about 50 cc. of water and heated to boiling. At about 75° a brown oil formed which became gradually coated with white crystals. By frequent shaking the oil was completely changed to this white mass, which floated throughout the liquid. After the addition of more water the liquid was boiled, then cooled, and the white mass filtered. This, after drying, melted sharply at 136° to 137°. It was insoluble in acid, but soluble in alcohol, ether, and alkali, showing a decided change from the original amine hydrochloride.

0.1562 gram substance gave 0.2844 gram CO_2 and 0.0682 gram H_2O.

	Calculated for $C_9H_{10}O_2NCl$.	Found.
C	50.09	49.66
H	4.68	4.75

The rearranged body may also be obtained if the hydrochloride is covered with water and allowed to stand for a number of days at ordinary temperature.

As this was the first of the rearranged bodies containing a chlorine atom that we had obtained, a synthesis of the body was undertaken. The method used was to treat 4-chlor-2-aminophenol with ethyl chlorformate at ordinary temperature. The hydrochloride of this amine has been described by Faust and Saame,[1] but we were unable to obtain the body entirely free from tin by their method. The following method was used:

Two grams 4-chlor-2-nitrophenol (m. p. 87°) were covered with 15 cc. concentrated hydrochloric acid and the calculated amount of granulated tin added slowly, the solution being warmed a little. After a short time a white precipitate formed. When the reduction was complete the contents of the vessel were cooled, the liquid decanted, and the solid redissolved in water. After the tin was precipitated with hydrogen sulphide the solution was evaporated and the pure hydrochloride crystallized out.

One gram of the hydrochloride was suspended in ether in a separatory-funnel, and a slight excess of sodium carbonate, dissolved in a very little water, added. The water solution was separated from the ether and the calculated amount (0.5 molecule) of ethyl chlorformate added in small quantities. After the ether had evaporated a residue remained which melted at 136°, and mixed with the urethane formed by rearrangement, as prepared above, it caused no depression of the melting-point. The other properties were also identical with those of the rearranged body. The urethane was found to be unusually stable on being heated. Two grams 3-chlor-6-oxyphenylurethane were placed in a small Anschütz distilling-

[1] Ann. Chem. (Liebig), Suppl., 7, 193 (1870).

flask and heated slowly in a metal-bath. Up to 200° there was very little decomposition. Above 200° decomposition began. Alcohol distilled over, and, tested, gave iodoform. The heating must be carried out very slowly and the temperature kept at 230° for a considerable time. No effort was made to distil the carbonyl body over into the neck of the Anschütz apparatus, but after the decomposition was complete the residue was allowed to solidify and was dissolved in sodium hydroxide solution. The anhydro base was reprecipitated with hydrochloric acid, filtered, and crystallized several times from hot water. White needles were obtained which melted at 184° to 185°. If the decomposition was not complete, mixtures were obtained which melted at from 122° to 155°. Analysis proved the body to be carbonyl-4-chlor-2-aminophenol.

0.3211 gram substance gave 24.28 cc. N at 22° and 742 mm.

	Calculated for $C_7H_4O_2NCl$.	Found.
N	8.28	8.40

o-Chlorphenol (b. p. 176°) was prepared from the mixture obtained by the chlorination of phenol. The method of Faust and Müller,[1] as improved by Varnholt,[2] was used. It was found that the repeated distillation spoken of by Faust and Müller, for separating the isomers, can be avoided if a Glinsky tube is used and the distillation carried on very slowly. A yield of about 30 per cent of the oil, boiling at 176°, was obtained.

To 50 grams of *o*-chlorphenol[3] more than the calculated amount of nitric acid (sp. gr. 1.36), which had been diluted with an equal volume of water, was slowly added. A red oil formed, which became solid after twenty-four hours. This was collected, washed, and distilled with steam. The body obtained was practically pure 6-chlor-2-nitrophenol.

6-Chlor-2-nitrophenyl ethyl carbonate was obtained as an oil which could not be solidified at —15°. At this temperature, however, the oil became very thick.

[1] Ann. Chem. (Liebig), 173, 303 (1874).
[2] J. prakt. Chem., [2], 36, 22 (1887).
[3] Ann. Chem. (Liebig), 173, 307 (1874).

Hydrochloride of 6-Chlor-2-aminophenyl Ethyl Carbonate, $C_2H_5O_2\overset{1}{C}O\overset{6}{C}_6H_3Cl\overset{2}{N}H_3Cl$.—One gram of the carbonate was reduced in the usual way. In ten or fifteen minutes the solution became clear, and in a short time, with the evolution of some heat, the entire mass solidified. From this mass the amine hydrochloride was obtained as in the previous preparations. It formed a voluminous precipitate, which melted with decomposition at 126° to 127°. It is soluble in alcohol, insoluble in water and alkali, and not very soluble in acid. The yield was 70 to 80 per cent.

0.1359 gram substance required 5.4 cc. N/10 $AgNO_3$.

	Calculated for $C_9H_{11}O_2NCl_2$.	Found.
Cl	14.06	14.11

5-Chlor-6-oxyphenylurethane, $\overset{5}{Cl}(\overset{6}{OH})C_6H_3\overset{1}{N}HCO_2C_2H_5$.—One gram of the hydrochloride was covered with about 50 cc. of water at 25°. It softened and collected in the bottom of the vessel in a large mass. Heated a little, it turned to a brown oil, and the oil gradually went into solution. On cooling, a white crystalline solid (needles) separated, which was soluble in alcohol, ether, and alkali, but insoluble in acid. The melting-point was 92° to 93°.

0.1722 gram substance gave 0.3136 gram CO_2 and 0.0745 gram H_2O.

	Calculated for $C_9H_{10}O_2NCl$.	Found.
C	50.09	49.68
H	4.68	4.81

p-Bromphenol was prepared by the freezing method of Hübner and Brenken,[1] as extended by Hand,[2] with this exception, however, that the purification was accomplished by distillation *in vacuo*. This was done because small yields were obtained when distilled at ordinary temperature, due to decomposition, caused by the presence of small quantities of moisture. At 60 mm. the *p*-bromphenol boiled at 150°.

4-Brom-2-nitrophenol (m. p. 88°) was prepared by the nitra-

[1] Ber. d. chem. Ges., 6, 171 (1873).

[2] Ann. Chem. (Liebig), 234, 136 (1886).

tion of *p*-bromphenol in glacial acetic acid solution with fuming nitric acid in the cold. When nitration was complete, the contents of the vessel were poured into water, filtered, washed with water, and distilled with steam. The pure body (m. p. 88°) was obtained from the barium salt.

4-Brom-2-nitrophenyl ethyl carbonate was obtained from an ethereal solution in large, transparent plates, which melted at 76°.

Hydrochloride of 4-Brom-2-aminophenyl Ethyl Carbonate, $C_2H_5O_1\overset{1}{C}O\overset{4}{C_6}H_3\overset{3}{Br}NH_2Cl$.—One gram of the above carbonate, in a small vessel, was covered with 15 cc. of concentrated hydrochloric acid. After cooling, an excess of granulated tin was slowly added. The reduction was allowed to proceed slowly, and too much heat was not allowed to generate from the reaction. After a short time a white solid, of delicate appearance, which could be distinguished from the nitro body, began to appear, and in the course of an hour the entire vessel was filled with a pure, white, solid mass. The best results were not obtained when the reduction was carried out in the cold. The temperature, however, was not allowed to rise above 20°. When the reduction was complete, the solid mass was cooled with a freezing-mixture and added slowly to a very cold solution of 50 grams of potassium hydroxide in 50 cc. of water, and the amine and its hydrochloride obtained in the usual way. The yield was 70 to 80 per cent; the melting-point was 136° to 137°.

0.1952 gram substance required 6.41 cc. N/10 $AgNO_3$.

	Calculated for $C_9H_{11}O_2NClBr$.	Found.
Cl	11.95	11.73

3-Brom-6-oxyphenylurethane, $\overset{3}{Br}(\overset{6}{OH})C_6H_3\overset{1}{N}HCO_2C_2H_5$. — One gram of the hydrochloride was covered with water and heated. Most went into solution at the boiling-point, and on cooling white needles, melting at 139° to 141°, were obtained. These were soluble in alcohol, ether, chloroform, and alkali, but insoluble in acid. The body may be prepared more quickly if the hydrochloride is dissolved in alcohol, a little

water added, and the mixture allowed to stand a short time at ordinary temperature. On addition of an excess of water, white needles, melting at 140° to 142°, are precipitated.

0.2407 gram substance gave 0.3636 gram CO_2 and 0.0869 gram H_2O.

	Calculated for $C_9H_{10}O_3NBr$.	Found.
C	41.52	41.20
H	3.88	4.01

In the preparation of 4-chlor-2-nitrophenol by the method of Faust and Saame[1] the crude material obtained in nitrating the chlorinated phenol was first changed into the barium salt by boiling with barium carbonate. The purpose was to separate the 6-chlor-2-nitrophenol from the 4-chlor-2-nitrophenol, advantage being taken of the different solubilities of their barium salts. The method did not effect a complete separation, so the barium salts were covered with water, precipitated with hydrochloric acid, washed, and the product distilled with a strong stream of steam. In the condenser a yellow deposit formed, which did not melt when the water surrounding it was brought to the boiling-point. It could not be, therefore, 4-chlor-2-nitrophenol (m. p. 87°), nor 6-chlor-2-nitrophenol (m. p. 70°). It was collected and found to melt sharply at 121° to 122°. This is the melting-point of 4,6-dichlor-2-nitrophenol, but as 4-nitro-2,6-dichlorphenol melts at 125°, it was necessary to distinguish between these bodies in another way. The ethyl ether was prepared by converting the dichlornitrophenol (m. p. 122°) into the silver salt and treating this with ethyl iodide. The product dissolved in alcohol and precipitated by water melted at 29°, which is the melting-point of the 4,6-dichlor-2-nitrophenol ethyl ether prepared by Fischer.[2] The sodium and barium salts were also prepared and corresponded in properties to those described by Fischer.

It seemed, therefore, that in the chlorination of phenol quite a quantity of 2,4-dichlorphenol is formed, and this was afterwards verified by the isolation of a quantity of 2,4-dichlor-

[1] *Loc. cit.*

[2] Ann. Chem. (Liebig), Suppl., 7, 188 (1870).

phenol (b. p. 209° to 210°), from the crude product obtained in the chlorination of phenol.

4,6-Dichlor-2-nitrophenyl ethyl carbonate was obtained from the phenol (m. p. 122°) as a yellow oil, which solidified on cooling to a slightly yellow body melting at 38° to 39°. The yield was not so large as in the case of the other nitrocarbonates and it has been found to be general in these experiments that where the hydroxyl group is surrounded, as in this body, by other groups, it is much more difficult to bring it into action with the acyl group—a fact which may be explained on the basis of stereochemical interference.

Hydrochloride of 4,6-Dichlor-2-aminophenyl Ethyl Carbonate, $C_2H_5O_2\overset{1}{C}O.C_6H_3\overset{4}{Cl}\overset{6}{Cl}\overset{2}{N}H_3Cl$.—Some difficulty was experienced in isolating the reduction-product of the carbonate because of the ease with which the former saponifies when brought into the cold alkaline solution. In different preparations different colorations were observed from red to green, and the products did not give good analytical results. With the following method a pure white salt was obtained. As it is better to work with small quantities, three reductions of 1 gram each were carried on at the same time. In each small vessel 1 gram of the carbonate was placed and covered with 12 cc. of concentrated hydrochloric acid. Granulated tin was added in small quantities and the vessels shaken. The flasks were not allowed to become warmer than 30° during the reduction. When the reductions were complete and the vessels cooled, a white solid mass formed. The concentrated acid was then decanted and the solid, which contained some tin, was added in small quantities to a very cold solution of 50 grams of potassium hydroxide in 50 cc. of water. The hydrochloride obtained from the dry ethereal extract was white and was washed with ether free from alcohol, but containing a little water. The hydrochloride was soluble in alcohol but insoluble in water, alkali, or acid. It melted with decomposition between 132° and 135°.

0.2111 gram substance, covered with water and heated, after cooling required 7.26 cc. N/10 $AgNO_3$.

	Calculated for $C_9H_{10}O_2NCl_3$.	Found.
Cl	12.32	12.21

3,5-Dichlor-6-oxyphenylurethane, $Cl_2(OH)C_6H_2NHCO_2C_2H_5$, is formed very rapidly by rearrangement of the amine when the hydrochloride is dissolved in alcohol and a little water added to the solution. After a short time an excess of water precipitates the urethane. It melts at 125°.

0.2344 gram substance gave 0.3685 gram CO_2 and 0.0791 gram H_2O.

	Calculated for $C_9H_9O_2NCl_2$.	Found.
C	43.20	42.88
H	3.64	3.76

The urethane was also prepared by the action of ethyl chlorformate on 4,6-dichlor-2-aminophenol. It melted at 125°, and mixed with the body prepared by rearrangement showed no depression of melting-point. The two bodies are identical.

Since 4,6-dichlor-2-aminophenyl ethyl carbonate showed such an unusual tendency to rearrange, thus emphasizing the tendency of negative groups to hasten the molecular change, it seemed of interest to gain some further evidence as to the combined action of negative groups upon the rearrangement. 4-Chlor-6-brom-2-nitrophenol was therefore prepared. Ten grams 4-chlor-2-nitrophenol (m. p. 87°) was dissolved in glacial acetic acid and brominated at a high temperature, according to the method of Ling.[1] In this manner a quantitative yield of 4-chlor-6-brom-2-nitrophenol (m. p. 125°) was obtained.

4-Chlor-6-brom-2-nitrophenyl Ethyl Carbonate.—A known weight of the phenol was dissolved in a little more than the calculated amount of potassium hydroxide solution, and to this red solution a slight excess of ethyl chlorformate was added slowly with shaking. As in other cases where the hydroxyl group is surrounded, the reaction with ethyl chlorformate was not rapid, but after much shaking a yellow oil formed. This was extracted with ether and on evaporation

[1] J. Chem. Soc. (London), **55**, 588 (1889).

yellow prisms remained. They were crystallized out of alcohol and melted at 48° to 49°.5.

Hydrochloride of 2-Amino-4-chlor-6-bromphenyl Ethyl Carbonate, $C_2H_5CO_2O.C_6H_2ClBrNH_2Cl$.—One gram of carbonate was treated with 12 cc. of concentrated hydrochloric acid and after cooling an excess of granulated tin was added. In a short time a flaky white substance began to form which clung to the sides of the vessel. The reduction in this case was slow, and it was not until after a considerable time that the yellow nitro body entirely disappeared. When the reduction was complete the entire contents of the vessel were poured slowly into 50 cc. of a very cold solution (1 : 1) of potassium hydroxide. The ethereal extract was red, and continued red after drying with solid potassium hydroxide. It was then filtered and dry hydrogen chloride passed in. The solution at first became colorless and no precipitate formed for some time, but finally, after considerable gas was passed in, a white precipitate formed. The yield was 60 per cent. The hydrochloride, filtered and washed with absolute ether and dried in a vacuum-desiccator, was analyzed (Analyses I. and II.).

The analysis did not give figures corresponding to the pure salt desired, and other preparations were made, using smaller quantities for the reduction and keeping the temperature very low and cooling the ether before making the extraction. In this manner the colorations of the ethereal solution were avoided, and the salt obtained purer than before, but not perfectly pure, as shown by the third analysis.

0.2312 gram substance required 8.9 cc. N/10 $AgNO_3$.
0.2145 gram substance required 7.56 cc. $AgNO_3$.
0.1921 gram substance required 6.01 cc. $AgNO_3$.

	Calculated for $C_9H_{10}O_2NCl_2Br$.	Found. I.	II.	III.
Cl	10.68	13.71	12.50	11.11

The salt melted with decomposition at 131° to 132°. It is insoluble in water.

3-Chlor-5-brom-6-oxyphenylurethane, $^{3}\mathrm{Cl}^{5}\mathrm{Br}^{6}(\mathrm{OH})\mathrm{C_6H_2}^{1}\mathrm{NHCOC_2H_5}$.—One-half gram of the hydrochloride was dissolved in alcohol, an equal volume of water added, and the whole allowed to stand for a short time. On adding an excess of water a white precipitate formed. This was soluble in alkali and insoluble in acid. It melted at 116° to 118°.

0.1909 gram substance gave 0.2566 gram CO_2 and 0.0605 gram H_2O.

	Calculated for $C_9H_{10}O_2NClBr$.	Found.
C	36.66	36.65
H	3.08	3.46

4,6-Dibrom-2-cresol (m. p. 57°), was prepared by the bromination of *o*-cresol in glacial acetic acid solution in the presence of small pieces of iron[1] wire. 4-Brom-6-nitro-2-cresol (m. p. 88°) was prepared from it by treatment in glacial acetic acid with sodium nitrite, the product being distilled with steam and finally crystallized out of alcohol, according to the method of Zincke.[2] It was found that a somewhat better yield can be obtained if the dibrom body is allowed to stand over night with a slight excess of sodium nitrite before the addition of water.

4-Brom-2-nitro-6-methylphenyl Ethyl Carbonate.—Five grams of the cresol (m. p. 88°) were dissolved in a small excess of potassium hydroxide solution, and a slight excess of ethyl chlorformate was slowly added. As before, where the hydroxyl group is surrounded, the reaction was slow, but a yellow oil finally separated which, on cooling, solidified. This contained some of the unchanged nitrophenol, as was shown by the red color produced by addition of alkali, and the variation of melting-point from 44° to 55°, after repeated crystallizations from alcohol. To obtain the pure body the substance was washed repeatedly with dilute potassium hydroxide solution and finally with water. It is soluble in alcohol, ether, and chloroform and melts at 61° to 62°.

[1] J. prakt. Chem., [2], 38, 325 (1888).

[2] We are under obligations to Prof. Th. Zincke, who very kindly placed the dissertation of Wagner, 1899, at our disposal.

Hydrochloride of 2-Amino-4-brom-6-methylphenyl Ethyl Carbonate, $C_2H_5O_2\overset{1}{C}O\overset{6}{C_6}H_2(\overset{}{C}H_3)\overset{4}{B}r\overset{2}{N}H_2Cl$.—One gram of the pure carbonate was covered with 15 cc. of concentrated hydrochloric acid and an excess of granulated tin added. The vessel was not heated, but no attempt was made to keep it cold. A white solid formed throughout the liquid and after some time collected at the top of the liquid. After the reduction was complete the entire mass was cooled and added slowly to 50 cc. of a 1 : 1 solution of potassium hydroxide which had been cooled to —10°. This was extracted several times with absolute ether and dried with solid potassium hydroxide. Dry hydrogen chloride gave a white precipitate. It was washed with absolute ether and dried on a clay plate in a desiccator. Heated, it darkened at 137° to 143°, but did not melt until 173° to 178°, and then with decomposition. The hydrochloride is soluble in alcohol and insoluble in water.

0.2031 gram substance required 6.54 cc. N/10 $AgNO_3$.

	Calculated for $C_{10}H_{13}O_2NClBr$.	Found.
Cl	11.41	11.43

3-Brom-5-methyl-6-oxyphenylurethane, $\overset{6}{(OH)}\overset{3}{B}r(\overset{5}{C}H_3)C_6H_2\overset{1}{N}HCO_2C_2H_5$.—One gram of the hydrochloride was placed in a flask and covered with about 50 cc. of water. The water did not seem to wet the body, as in the case of the isomer, which will be described later. When heated, however, it went into solution more readily than the isomer. When cooled, a white solid separated, which was soluble in alkali and had the same general properties as the other urethanes which had already been prepared. The melting-point was 123°.

0.2127 gram substance gave 0.3392 gram CO_2 and 0.0873 gram H_2O.

	Calculated for $C_{10}H_{12}O_2NBr$.	Found.
C	43.77	43.5
H	4.42	4.56

2,6-Dibrom-4-cresol (m. p. 49) was prepared from *p*-cresol

by bromination in glacial acetic acid solution with the calculated amount of bromine, according to the method of Glaus and Jackson.[1]

Ten grams of the brominated cresol were dissolved in a small amount of glacial acetic acid and slowly a slight excess of sodium nitrite was added. After a short time a yellow precipitate formed. When the reaction was complete, the contents of the vessel were poured into a large bulk of water, filtered, and washed. The yellow crystalline mass, after crystallization from alcohol, melted at 69°, and was 2-nitro-6-brom-4-cresol.

This body was also prepared from 2-nitro-4-cresol[2] by bromination with potassium bromate and an acid solution of potassium bromide. The yield, however, in this case was not so good as by the first method.

2-Nitro-4-methyl-6-bromphenyl Ethyl Carbonate.—Five grams of nitrobromcresol (m. p. 69°) were dissolved in slightly more than the calculated amount of potassium hydroxide solution, and slowly a small excess of ethyl chlorformate was added. A yellow solid formed which melted at from 65° to 75°. On shaking out with dilute potassium hydroxide solution the melting-point became constant at 84° to 85°. The reactivity of the ethyl chlorformate is here also interfered with, because of the enclosed position of the hydroxyl group, and a quantitative yield was not easily obtained.

Hydrochloride of 2-Amino-4-methyl-6-bromphenyl Ethyl Carbonate, $C_2H_5O_2\overset{1}{C}O\overset{2}{C_6}H_2(\overset{4}{C}H_3)\overset{6}{B}r\overset{3}{N}H_2Cl$.—One gram of the carbonate (m. p. 84°) was covered with 15 cc. concentrated hydrochloric acid and an excess of granulated tin added. The reduction was carried on at ordinary temperatures. When reduction was complete the contents of the vessel were treated as usual. The hydrochloride obtained from the ethereal solution was washed with absolute ether and dried on a clay plate in a desiccator. It is insoluble in water, but soluble in ether, to which a little alcohol has been added. The substance melted at 142° to 143°, with decomposition.

[1] *Loc. cit.*

[2] Thiele and Eichwede: Ann. Chem. (Liebig), 311, 375 (1900).

0.2311 gram substance required 7.43 cc. N/10 $AgNO_3$.

	Calculated for $C_{10}H_{13}O_3NClBr$.	Found.
Cl	11.41	11.40

3-Methyl-5-brom-6-oxyphenylurethane, $\overset{3}{C}H_3\overset{5}{Br}(\overset{6}{O}H)C_6H_2\overset{1}{N}HCO_2C_2H_5$.—One gram of the hydrochloride was heated with about 50 cc. of water. A brown oil formed which did not go entirely into solution. Upon cooling, the oil solidified and melted at 83°. It was soluble in alcohol, ether, and alkali, but insoluble in acid.

0.2100 gram substance gave 0.3357 gram CO_2 and 0.0822 gram H_2O.

	Calculated for $C_{10}H_{13}O_3NBr$.	Found.
C	43.77	43.60
H	4.42	4.35

PART IV.

2-Amino-4-chlorphenyl Acetate.

Hübner and Stünkel,[1] in reducing *o*-nitrophenyl benzoate with a view to obtaining *o*-aminophenyl benzoate, found that from the alcoholic solution in which the reduction was carried on, an anhydrobenzenyl-*o*-aminophenyl base was in every case obtained. This compound, when boiled with water, went over into benzoyl-*o*-aminophenol. They ascribed the formation of the anhydro base as a primary product, instead of the expected aminophenyl benzoate to the great instability of the amino bodies.

Böttcher,[2] in repeating the work of Hübner and Stünkel, observed that by varying the temperature at which the experiment was carried out either the anhydro base or the benzoyl-*o*-aminophenol could be obtained at will. He suggested the following stages for the reaction:

$$O_2NC_6H_4OCOC_6H_5 \rightarrow C_6H_5\underbrace{C : N.C_6H_4O} \rightarrow C_6H_5CO.NHC_6H_4OH.$$

[1] Ann. Chem. (Liebig), 210, 384 (1881).
[2] Ber. d. chem. Ges., 16, 631 (1883).

In a later work Böttcher,[1] trying to determine if this rearrangement is a perfectly general one, tried, among other experiments, a reduction of *o*-nitrophenyl acetate, thinking that the anhydro base, ethenylaminophenol would in like manner be formed. Trying the reduction with alcoholic ammonia and hydrogen sulphide in the cold, with tin and hydrochloric acid, and with zinc and acetic acid, he was unable to obtain either acetylaminophenol, the anhydro base, or aminophenyl acetate, as he thought, on account of the saponification of *o*-nitrophenyl acetate, in the process of the reduction, the acetate being supposedly much more unstable than the benzoate.

The experiments with the hydrochloride of 4-chlor-2-aminophenyl ethyl carbonate, which have been described above, and the surprising insolubility of this salt in water, suggested that if the chlorine in the para position should effect a similar insolubility of an acetate, it might be possible to prepare the hydrochloride of 4-chlor-2-aminophenyl acetate as the first body of its kind ever isolated. A study of it would determine the real nature of the processes by means of which an anhydro base or an acylaminophenol was always obtained by the reduction of the nitrophenyl acetates and benzoates. By the observation of minute precautions we have been able to isolate the hydrochloride of 2-amino-4-chlorphenyl acetate, although it proved to be readily soluble in water. In contact with water, it produces acetyl-2-aminochlorphenol, not by the successive loss and addition of water with the intermediate formation of an anhydro base, but by a molecular rearrangement according to

$$CH_3COOC_6H_3ClNH_3Cl \rightarrow HOC_6H_3ClNHCOCH_3 + HCl.$$

The free base, aminochlorphenyl acetate, was also obtained from its salt and observed to change spontaneously into the isomeric phenol. The anhydro base was prepared by the action of heat on acetylaminochlorphenol and compared with the amine.

4-Chlor-2-nitrophenyl Acetate.—Ten grams of 4-chlor-2-ni-

[1] Ber. d. chem. Ges., **16**, 1933 (1883).

trophenol (m. p. 87°) were put in a flask with fused sodium acetate and an excess of acetic anhydride added. The mixture was heated for more than an hour, above 100°, in an air-bath, and shaken from time to time. On cooling, the entire mass solidified. It was covered with water, and an oil formed at the bottom of the vessel. After the water solution had been removed, the oil was washed several times with dilute potassium hydroxide solution, to dissolve any unchanged phenol. When placed in ice-water the oil solidified to an almost white solid. 4-Chlor-2-nitrophenyl acetate is quite soluble in benzol, chloroform, and ether, fairly soluble in alcohol, and may be precipitated from alcohol solution by water. It melts between 47° and 48°. It was identified by the reduction to

The Hydrochloride of 4-Chlor-2-aminophenyl Acetate, $ClNH_2C_6H_3ClOCOCH_3$.—In the first attempt to reduce the acetate, 1 gram was covered with 10 cc. concentrated hydrochloric acid, and more than the calculated amount of granulated tin was added in small quantities to the cold solution, which was kept at about 0°. After some time the solution became clear and was poured slowly into a solution of 50 grams of potassium hydroxide in 50 cc. water which had been cooled to —10° C. When the concentrated acid solution went into the cold potassium hydroxide, drop by drop, fumes arose which indicated a decomposition. The potassium hydroxide solution was extracted several times with ether, the extract dried with solid potassium hydroxide, filtered, and treated with dry hydrogen chloride; no precipitate was formed, and on evaporation to dryness no residue remained. It was evident that nothing had been taken up by the ether.

A second experiment was carried out exactly as above, with this exception, that a deep layer of absolute ether was placed over the potassium hydroxide solution. The ether and alkali were then cooled to —10° C. The cold acid solution containing the reduced product was poured, drop by drop, through glass wool upon the ether and shaken after each addition, the temperature not being allowed to rise above —5° C. The ether was decanted into a cold vessel containing

some solid potassium hydroxide and two similar extraction with cold ether were made. After being dried for some time,[8] the ethereal solution was filtered into another cold vessel and dry hydrogen chloride run in. A pure white hydrochloride formed in a short time, which was filtered and placed on a clay plate in a vacuum-desiccator. Put into water, it went into solution for an instant, but then a white, oily body came out, insoluble in alkali, but soluble in concentrated acid. On standing in water for more than a day, it became crystalline, and was soluble in alkali, no longer soluble in acid, and melted at 176°. The hydrochloride, on the other hand, melts at 105° to 107°. It had been converted by a molecular rearrangement into acetyl-2-amino-4-chlorphenol, which, as will be shown below, melts at 176°. In the analysis of the hydrochloride it was warmed with some water to cause the rearrangement and the liberated hydrochloric acid was then titrated with standard alkali.

0.2468 gram substance (dried for twenty-four hours) required 10.64 cc. N/10 NaOH.

0.3222 gram substance (dried for two hours) required 14.02 cc. N/10 NaOH.

	Calculated for $C_8H_9O_2NCl_2$.	Found. I.	II.
Cl	15.96	15.40	15.52

The analysis indicated that the hydrochloride of 2-amino-4-chlorphenyl acetate had been isolated. As it gave a somewhat low chlorine value and the hydrochlorides of anhydro bases, which had hitherto always resulted from reductions of *o*-nitrophenyl acetates, have a well-known tendency to lose hydrochloric acid on standing, further evidence of the identity of the amine hydrochloride was sought. Its identity was confirmed by the preparation of a chlorplatinate and fully established by the preparation and study of the hydrochloride of the anhydro base itself. As expected, the latter proved to be quite a different body from the salt described above. The free bases were prepared from the two salts and also found to be different compounds, and the aminochlorphenyl acetate obtained from the hydrochloride, which has just been described,

rearranged spontaneously into the isomeric acetylaminochlorphenol. In view of these facts the salt obtained as the first product of the reduction of the nitro compound has undoubtedly the constitution assigned to it.

A chlorplatinate of the base was obtained by the addition of a concentrated solution of chlorplatinic acid in absolute alcohol to a cold ethereal solution of freshly prepared amine. The yellow precipitate was washed with ether containing some alcohol and dried on a clay plate. It is insoluble in water, and rubbed with water no change of color or apparent decomposition takes place. It darkens at 120° and does not melt at 200°.

0.0256 gram substance gave 0.0064 gram Pt.

	Calculated for $C_{16}H_{18}O_4N_2PtCl_8$.	Found.
Pt	24.95	25.00

2-Amino-4-chlorphenyl Acetate, $H_2N.C_6H_3Cl(OCOCH_3)$.—A little of the ethereal solution of the amine, prepared as described above, was allowed to evaporate. White needles, turning a little red on standing in the air, remained. They melted at 73° to 74°. The addition of some of the anhydro base, described below, whose melting-point is 54°, lowered the melting-point of the amine below 40°. The amine is soluble in acids, insoluble in alkalies, soluble in chloroform and benzene, but not very soluble in low-boiling ligroin. The base was allowed to stand for a day and the melting-point again taken. The substance fell together a little at 73°, but it did not melt until 176°, the melting-point of acetylaminochlorphenol. The aminochlorphenyl acetate had evidently suffered a molecular rearrangement according to

$$CH_3COOC_6H_3ClNH_2 \rightarrow HOC_6H_3ClNHCOCH_3.$$

Acetyl-2-amino-4-chlorphenol, $CH_3CONH.C_6H_3Cl(OH)$.—In an endeavor to prepare a quantity of the rearranged body melting at 176°, for purposes of analysis and further investigation, some surprising results were obtained. Two grams of the 4-chlor-2-nitrophenyl acetate were reduced with powdered tin and concentrated hydrochloric acid, the solution be-

ing kept cold, as above. After all had gone into solution it was poured through glass wool into about two volumes of water at ordinary temperature. The entire vessel of water became milky white, and when filtered, the filter-paper was covered with a white, thick, oily substance. The oil was insoluble in alkali, fairly soluble in concentrated acid, and when rubbed with alcohol and ether went into solution. When some of the oil placed in a test-tube was dissolved in ether and dry hydrogen chloride run in, a white precipitate formed. This hydrochloride is not soluble in water and turns brown on standing in the air. Heated in a melting-point tube, it became brown below 100° C., but did not melt until 233° to 235° C. If allowed to stand for more than a day in water, it became crystalline and melted sharply at 176° C. We expect in a later work to investigate the oil more carefully. It may be an intermediate product in the rearrangement of the amine. Its evident impurity and the fact that it contains inorganic matter, led us to abandon it here as not leading to a direct knowledge of the identity of the supposed 4-chlor-2-aminophenyl acetate. An analysis of the body melting at 176° was made.

0.2748 gram substance gave 0.5188 gram CO_2 and 0.1088 gram H_2O.

	Calculated for $C_8H_8O_2NCl$.	Found.
C	51.73	51.48
H	4.35	4.40

The body is soluble in alkali and reprecipitated by acid and is undoubtedly acetyl-2-amino-4-chlorphenol. It was also prepared synthetically as follows: One gram of the hydrochloride of 2-amino-4-chlorphenol was mixed thoroughly with 1 gram of fused sodium acetate and covered with 3 grams of acetic anhydride. This mixture was heated to boiling under an inverted condenser for four hours. On adding water, a part did not go into solution, and this, on purification, melted at 176° C. Mixed with the acetyl body prepared by the above method, it caused no depression of the melting-

point. It had also, in other respects, the properties of acetyl-2-amino-4-chlorphenol.

Ethenyl-4-chlor-2-aminophenol, $CH_3C:N.C_6H_3ClO$. — The anhydro base was prepared for comparison of its hydrochloride with the hydrochloride of 4-chlor-2-aminophenyl acetate. One gram acetyl-2-amino-4-chlorphenol was placed in an Anschütz distillation-bulb and heated carefully. It melted at 176° and soon afterward drops of water were given off which collected in the side tube. At 218° to 220° the anhydro base distilled over. The distillate was poured upon a watch-crystal and placed over solid potassium hydroxide in a vacuum-desiccator. White needles formed at once. They melted sharply at 53° to 54°. These crystals have a peculiar, pleasant odor. They are soluble in dilute acid, insoluble in alkali, soluble in ether, alcohol, benzene, and chloroform. One-half gram was dissolved in absolute ether and dry hydrogen chloride run in. After some time a white precipitate formed. This was filtered, washed with absolute ether, and dried. This hydrochloride is soluble in dilute acid, insoluble in alkali, and not very soluble in water. It is soluble in alcohol and chloroform, but very little soluble in benzene. It does not give the peculiar milky appearance shown by the hydrochloride of 4-chlor-2-aminophenyl acetate when covered with water. It melted at 129° to 130°.5.

0.1928 gram of the hydrochloride was weighed at once after precipitation, covered with water, and the acid titrated with N/10 sodium hydroxide.

	Calculated for $C_8H_7ONCl_2$.	Found.
Cl	17.37	17.34

This hydrochloride gave off hydrogen chloride on standing, and, after two days, again melted at 53° to 54°, having returned to the anhydro base. The hydrochloride was mixed with the hydrochloride of 4-chlor-2-aminophenyl acetate. The mixture melted below 100° C.

The anhydro base (0.25 gram) was dissolved in absolute ether and chlorplatinic acid in absolute alcohol solution added.

The yellow precipitate was filtered and washed with ether containing some alcohol. The chlorplatinate is with difficulty soluble in alcohol, insoluble in benzol, chloroform, and ligroin. Covered with water and rubbed, it turned white with evident decomposition. Heated in a melting-point tube, it did not darken or melt at 220° C.

0.0202 gram chlorplatinate gave 0.0053 gram Pt.

	Calculated for $C_{16}H_{14}O_2N_2PtCl_6$.	Found.
Pt	26.16	26.20

The evidence is conclusive that with proper precautions an *o*-aminophenyl acetate can be isolated as the primary reduction-product of the *o*-nitrophenyl acetates. Hübner, Stünkel, Böttcher, and others, who have studied the reduction of these bodies, failed to obtain the amines, most likely because heat was probably allowed to generate during the reduction, with a consequent change of the amine by rearrangement into the oxyacetanilide or by a loss of water into an anhydro base.

I wish here to express my thanks to Professor Stieglitz for the careful attention he has given to each part of this work.

THE ACTION OF HYDROGEN PEROXIDE UPON ANHYDRIDES AND THE FORMATION OF ORGANIC ACID, PEROXIDES, AND PERACIDS.

By A. M. Clover and A. C. Houghton.

Nef[1] has shown that pure hydrogen peroxide and acetic anhydride reacting with each other yield acetic peroxide. Baeyer[2] found that the same substance was formed by the action of acetic anhydride upon an aqueous solution of hydrogen peroxide. Neither of these authors attempt to explain the reaction which takes place and one might be led to suppose that the peroxide was formed by the direct addition of oxygen to the anhydride. In considering the reaction of hydrogen peroxide upon benzoyl acetyl oxide, however, Nef assumes the following reaction to take place:

[1] Ann. Chem. (Liebig), **298**, 287.
[2] Ber. d. chem. Ges., **33**, 1569.

$$\begin{matrix} C_6H_5CO \\ CH_3CO \end{matrix} O + \begin{matrix} HO \\ HO \end{matrix} = \begin{matrix} CH_3COO \\ C_6H_5COO \end{matrix} + H_2O.$$

In attempting to prepare other peroxides by the action of anhydrides upon hydrogen peroxide we have found that only the anhydrides of the simple acids react with hydrogen peroxide, *i. e.*, anhydrides which are acted upon by water. Even when the more complex and less soluble anhydrides are brought together with hydrogen peroxide in ethereal solution, there is no reaction.

From experimental facts which will be brought out later in this article, it will be seen that the action of hydrogen peroxide upon anhydrides is not a simple one: that the reaction is very similar to that of water upon anhydrides, and the formation of peroxides depends upon two distinct reactions.

Changes in Acetic Peroxide when Dissolved in an Aqueous Solution of Hydrogen Peroxide.

The changes which an aqueous solution of acetic peroxide undergoes have been previously studied by one of the authors in connection with G. F. Richmond.[1] It was found that the substance was hydrolyzed with the formation of acetic acid and acetic peracid, and it was shown that acetic peracid could be distinguished from acetic peroxide by its very rapid action upon potassium iodide. The action of acetic peroxide in dilute solution upon potassium iodide, if the latter be not in large excess, is so slow that the iodine liberated by the peracid may be estimated with little error.

We have found that when acetic peroxide is dissolved in a solution of hydrogen peroxide there is a similar change into peracid, but that the amount of peracid in the solution is more than can be accounted for by the reaction of the peroxide upon water; moreover, that there is a gradual loss of hydrogen peroxide in the solution, the active oxygen of which is found combined with the acetyl group. In order to follow these changes, it is necessary to be able to accurately esti-

[1] This JOURNAL, **29**, 179.

mate hydrogen peroxide, acetic peroxide, and acetic peracid in the presence of each other.

In dilute solutions containing no mineral acid, the action of hydrogen peroxide, as well as acetic peroxide, upon potassium iodide, is so slow that with practice one may accurately estimate peracid by adding a drop or two of strong potassium iodide solution and titrating immediately with thiosulphate. If only a small amount of potassium iodide is added, there need be no especial hurry in making the titration; after the removal of the "immediate" iodine, the further liberation can be seen to be very slow. If too much potassium iodide is used it is necessary to operate quickly and to make a preliminary titration to obtain approximately the amount of thiosulphate required; the estimation may then be made quickly. In either case, after a little practice, one may satisfy himself of the accuracy of the result.

The estimation of hydrogen peroxide may be accurately made by adding to a large excess of dilute sulphuric acid (2N acid was used) and titrating with permanganate. It has been previously shown that peracids oxidize manganous salt to permanganic acid, and that this action interferes with the estimation as ordinarily made; however, in very dilute solution, which is strongly acidified, this action is so retarded that there is little error.

The following experiments illustrate the accuracy of the method:

Ten cc. of a solution of commercial hydrogen peroxide titrated with N/20 permanganate in the ordinary manner required 23.7 cc. A strong solution of pure acetic peroxide[1] was made and allowed to stand for four hours. At the end of this time the peracid in 1 cc. of the solution was represented by 6.1 cc. N/20 thiosulphate; the unchanged peroxide by 6.6 cc. Only a trace of hydrogen peroxide had been developed.

Separate portions, of 10 cc. each, of the above solution of

[1] The acetic peroxide used in this work was prepared according to the method of Clover and Richmond (*Loc. cit.*) and was recrystallized from ligroin just before using.

hydrogen peroxide were then each diluted to 300 cc. with dilute sulphuric acid and cooled to 10°. To the first was then added 1 cc. of the above solution of acetic peroxide and peracid, to the second 2 cc., to the third 3 cc., and to the fourth 4 cc. These solutions were then titrated with N/20 permanganate.

	Required. cc.
1	23.65
2	23.60
3	23.65
4	23.55

In the fourth solution the amount of active oxygen as peracid was nearly equal to that as hydrogen peroxide. To obtain accurate results it is necessary to make the titration quickly, and to do this it is necessary, in case the amount of hydrogen peroxide in the solution is unknown, to make a preliminary titration in order to obtain approximately the volume of permanganate required.

The acetic peroxide cannot be directly estimated, but may be obtained by difference after estimating the total active oxygen. This may be accurately done by dissolving in a small amount of 20 per cent acetic acid containing potassium iodide and allowing to stand for a half hour, then diluting and titrating with thiosulphate. Careful experiments with known quantities of hydrogen peroxide, acetic peroxide, and acetic peracid have shown that all of these substances may be accurately estimated in this way. A correction obtained from a blank solution may be applied.

A solution of commercial hydrogen peroxide containing 30.5 grams per liter was nearly saturated with pure acetic peroxide. The contents of the solution were estimated as quickly as possible after it was made and then at intervals. The temperature of the solution remained constant, 23°.

For the estimation of hydrogen peroxide 1 cc. of the solution was removed and diluted to 100 cc. Fifty cc. of this were removed, and after diluting to 300 cc. with dilute sulphuric acid, were titrated with N/20 permanganate, as already described. This number multiplied by 2 is the one given in the table.

For the estimation of peracid, 1 cc. of the solution was added to 300 cc. of water, a small amount of potassium iodide solution added, and the iodine liberated was titrated quickly with N/20 thiosulphate.

The total active oxygen contained in 1 cc. of the solution was determined by dissolving in 6 or 7 cc. of a 20 per cent solution of acetic acid containing potassium iodide, and allowing to stand for one-half hour. The solution was then diluted and the free iodine estimated with N/20 thiosulphate. Only a slight correction, amounting to about 2 drops of thiosulphate, is necessary.

The three portions to be estimated were removed from the original solution as quickly as possible after each other. After being diluted as described no further change takes place in the diluted solution during the time necessary to carry on the estimations.

Time in hours.	N/20 thiosulphate (immediate). cc.	N/20 thiosulphate total. cc.	N/20 permanganate. cc.	N/20 thiosulphate representing acetic peroxide. cc.
..	..	48.5	35.0	13.5
2	6.7	48.0	31.7	9.6
7	12.7	47.5	28.8	6.0
24	13.9	46.1	27.8	4.4

An inspection of these figures brings out the following facts:

(1) At the end of two hours the amount of active oxygen as peracid in the solution is just one-half of that originally present as peroxide. The formation of peracid is, therefore, much faster than in aqueous solution.[1]

(2) The amount of hydrogen peroxide in the solution rapidly decreases; further, the solution gradually loses in total active oxygen, but the loss in hydrogen peroxide is much greater than the loss in total active oxygen.

(3) At each interval the total active oxygen present as peroxide and peracid is considerably greater than that originally present as peroxide. Acetic peracid is, therefore, formed

[1] Clover and Richmond: *Loc. cit.*

at the expense of the active oxygen of the hydrogen peroxide.

The solution of hydrogen peroxide employed contained a small amount of soluble mineral matter, which has a much greater catalytic action upon acetic peracid than upon hydrogen peroxide. This partly accounts for the loss in active oxygen; however, this loss was greatest during the first stages of the reaction at the time when the amount of peracid was smallest. Active evolution of oxygen in the solution was most noticeable during the first hour or two. The greater part of the loss is, therefore, intimately connected with the reaction itself. During the last stages of the reaction the peracid is evidently decomposed faster than it is formed.

The action of hydrogen peroxide upon acetic peroxide resulting in the formation of more peracid than would be formed by the ordinary hydrolysis, is most easily explained as follows:

$$\begin{matrix} CH_3COO \\ CH_3COO \end{matrix} \Big\rangle O + \begin{matrix} H \\ OOH \end{matrix} = 2CH_3COOOH.$$

Owing to the instability of the substances in question it is not possible to say that they react in the proportion indicated. The reaction suggests that of water upon acetic peroxide. Looked on in this light the possibility of a reaction, according to the following equation, suggests itself:

$$\begin{matrix} CH_3COO \\ CH_3COO \end{matrix} \Big\rangle O + \begin{matrix} H \\ OOH \end{matrix} = CH_3COOH + CH_3COOOOH.$$

Assuming such a reaction to take place, the loss of oxygen, already referred to, would be accounted for by the instability of the substance $CH_3COOOOH$, a derivative of the hypothetical trioxide of hydrogen.

A number of experiments, similar to the one described, were carried out with different solutions of hydrogen peroxide, and in all cases the same general results were obtained.

Action of an Aqueous Solution of Hydrogen Peroxide upon Acetic Anhydride.

When acetic anhydride is dissolved in hydrogen peroxide solution both acetic peracid and peroxide are soon present in the solution. The peracid in the solution may result from the hydrolysis of previously formed peroxide, or it may be formed directly by the action of hydrogen peroxide upon anhydride. A study of the rates of formation of these two substances has led to the conclusion that the peracid is the first substance formed.

The rate of formation of peracid in solutions of hydrogen peroxide of different strength is shown in the table given below. The best commercial hydrogen peroxide was used, which was concentrated to the strength given by distillation in a vacuum. The acetic anhydride was fractionated before using.

Twenty cc. of hydrogen peroxide solution (61.6 grams per liter) were brought to a temperature of 21° and 1 cc. of acetic anhydride added. The latter was dissolved quickly by shaking and the solution was kept at 21°. At different intervals, 1 cc. of the resulting solution was removed and the peracid present estimated in the manner already described. As the intervals of time are necessarily small, on account of the rapidity of the reaction, it was necessary to fill the pipette just before the time indicated and at the proper time to deliver the solution into a large volume of water, in order to stop or greatly retard any further reaction between the constituents. The results obtained appear in the first column below. In the second column are the results of a duplicate experiment carried out in exactly the same manner.

A solution of hydrogen peroxide of different strength (45.4 grams per liter) was also employed. The experiments with this solution were carried out in exactly the same way as described above, all conditions and measurements being the same. The results duplicated are placed in columns III. and IV.

Time in minutes.	I. N/20 thiosulphate.	II. N/20 thiosulphate.	III. N/20 thiosulphate.	IV. N/20 thiosulphate.
3	1.0	1.0	0.7	0.75
6	1.4	1.3	0.9	0.9
9	1.6	1.5	1.0	1.0
12	1.7	1.65	1.1	1.1
15	1.8	1.75	1.2	1.2
18	1.9	1.95		
21		2.2		
27		2.5		
30		2.6		

It will be noted that the rate of formation of peracid is large at first, but is soon checked. So long as acetic anhydride is present in the solution there would be a limit to the concentration of peracid owing to the ready reaction between the two substances.[1]

As soon as anhydride is removed from the solution, the formation of peracid by the hydrolysis of peroxide should continue at a uniform rate. To determine whether or not the relatively large amounts of peracid present in the solution at the earlier intervals can be accounted for by the hydrolysis of peroxide present, necessitates a determination of the amount of the latter substance in the solution at different intervals.

The amount of acetic peroxide was obtained as in the previous case, by subtracting from the total active oxygen the sum of the active oxygen as hydrogen peroxide and as peracid. The total active oxygen was obtained in the manner already described. The hydrogen peroxide was also estimated as previously described. Careful experiments showed that a known amount of hydrogen peroxide could be accurately estimated under the conditions employed and in the presence of the maximum amount of peracid, peroxide, and anhydride which might be in the solution to be examined. As this determination is of vital consequence to the results obtained and the conclusions drawn, a few of these experiments will be given.

A definite volume of hydrogen peroxide solution was estimated in the usual manner with N/20 permanganate. Required, 16.8 cc.; duplicated, 16.85 cc.

[1] Clover and Richmond: *Loc. cit.*

The same volume of hydrogen peroxide was added to 250 cc. of dilute sulphuric acid (2N) and again estimated. Required, 16.85 cc.; duplicated, 16.85 cc.

The same volume of hydrogen peroxide was added to 250 cc. of dilute sulphuric acid (2N). 0.05 gram of acetic anhydride was added, together with a solution of acetic peroxide, which had stood four or five hours and was equivalent to 4 cc. N/20 thiosulphate "immediate," and 9 cc. total. Required, 16.85 cc. permanganate.

The estimation of acetic peroxide in this manner is dependent upon three other determinations, each of which is liable to a reasonable experimental error. The numbers obtained are, therefore, approximate ones, but are all that can be desired.

The following experiments were made with the same solutions of hydrogen peroxide as were previously employed in the estimation of peracid, and were carried out in exactly the same manner, care being taken to make all conditions and measurements the same. The portion to be estimated for hydrogen peroxide was delivered into 500 cc. of water at the proper time. Only a portion of this was titrated, the numbers appearing in the table representing the entire amount. It was not necessary to remove the portion to be estimated for total active oxygen at exactly the time indicated, as there is little variation in this value, during the time of the experiment. The figures in the table represent the amounts of N/20 solutions required by 1 cc. of the reaction mixture:

Hydrogen Peroxide, 61.6 Grams Per Liter.

Time in minutes.	Total thiosulphate.	Immediate thiosulphate.	Permanganate	Thiosulphate representing peroxide.
3	68.7	1.0	66.95	0.75
6	68.8	1.35	66.1	1.35
18	68.7	1.9	64.4	2.4
30	68.9	2.6	64.2	2.1

Hydrogen Peroxide, 45.4 Grams Per Liter.

Time in minutes.	Total thiosulphate.	Immediate thiosulphate.	Permanganate.	Thiosulphate representing peroxide.
3	51.0	0.7	49.9	0.4
6	50.8	0.9	48.1	1.8
18	50.8	1.3	46.65	2.85

Repetition of these experiments a number of times gave values which varied within a comparatively narrow range for reasons already mentioned. In no case, however, were the numbers found to exceed those given by more than 1.0.

Experiments were made to determine the rate of hydrolysis of acetic peroxide in a solution of hydrogen peroxide. The solutions of hydrogen peroxide used were the same as in the previous experiments. A solution of acetic peroxide (approximately N/5) was made by dissolving 1.2 grams of pure acetic peroxide in 100 cc. of hydrogen peroxide. This concentration of acetic peroxide is considerably greater than that at any time in either of the solutions examined. The temperature remained at 21°. The peracid in 1 cc. of the solution was estimated at intervals in the usual manner. The amount is represented in the tables below by N/20 thiosulphate, column I. representing the stronger solution of hydrogen peroxide and column II. the weaker:

Time in minutes.	I.	II.
2	0.2	0.2
4	0.3	0.3
8	0.45	0.4
16	0.8	0.6

These numbers are to be compared with those obtained for peracid in the previous experiments. It is evidently impossible to account for the amount of peracid in those solutions, assuming that it is formed by the hydrolysis of acetic peroxide. The comparison applies especially to the earlier stages of the reaction. It is known that later acetic peroxide is formed in considerable amount, and that this eventually hydrolyzes to peracid.

To make sure that the acetic acid present in the original experiment had no accelerating action on the rate of hydrolysis of the peracid, the reactions were compared in hydrogen peroxide solution of about 5.5 per cent, and in a 10 per cent acetic acid solution, containing the same concentration of hydrogen peroxide. The same amount of pure acetic peroxide was added to each solution. The amounts of peracid

formed at intervals in 1 cc. of the solutions as represented by N/20 thiosulphate are given below:

Time in minutes.	Acetic acid solution.	Unacidified solution.
20	0.3	1.1
40	0.6	1.8
60	0.8	2.3

It will be seen that the acid has a retarding rather than an accelerating influence.

It is evident that acetic peracid results directly from the action of acetic anhydride upon hydrogen peroxide, probably according to the following equation:

$$\begin{matrix} CH_3CO \\ CH_3CO \end{matrix} O + \begin{matrix} H \\ OOH \end{matrix} = CH_3COOH + CH_3COOOH.$$

This reaction is analogous to that of acetic peroxide upon hydrogen peroxide, already considered. Here again, we must notice the similarity between the action of hydrogen peroxide and ordinary hydrolysis by means of water.

One of us has previously shown[1] that peracids, even in very dilute solutions, are extremely reactive toward substances capable of ordinary hydrolysis. It was shown that either benzoic or acetic peracids could be almost completely converted into benzoic acetic and acetic peroxides, respectively, even in very dilute aqueous solution, by the addition of a small amount of acetic anhydride to the solution. The formation of the peroxide is, therefore, to be explained by the action of peracid upon unchanged anhydride. The great tendency for these substances to react is seen in the sudden check in the rate of formation of peracid during the reaction of acetic anhydride upon the solution of hydrogen peroxide.

Propionic anhydride was also found to show the same general behavior toward hydrogen peroxide as acetic anhydride. Its action is slower, but on account of its sparing solubility it is less suitable for study.

Since acetic peroxide is almost completely changed to peracid in the course of twenty-four hours, experiments were

[1] *Loc. cit.*

made to determine the practicability of preparing a solution of acetic peracid by allowing a solution of anhydride in hydrogen peroxide to stand for this length of time.

(1) Two cc. of acetic anhydride were added to 100 cc. of a 3.2 per cent commercial hydrogen peroxide solution, and kept cool by immersing in a vessel of water. After twenty-four hours the total amount of peracid in the solution estimated in the usual manner was 0.33 gram. From this it follows that about 22 per cent of the anhydride entered into reaction with hydrogen peroxide.

(2) Five cc. of acetic anhydride were added to 100 cc. of the same hydrogen peroxide solution and kept cool. After twenty-four hours the solution contained 0.82 gram peracid. Here again, 22 per cent of the anhydride entered into combination with the hydrogen peroxide.

(3) Ten cc. of anhydride were added to 100 cc. of the same hydrogen peroxide solution, and kept cool. After twenty-four hours there were 1.54 grams of peracid in the solution. In this case 21 per cent of the anhydride entered into reaction with the hydrogen peroxide.

These experiments bring out an important fact; namely, that the rate of the reaction of hydrogen peroxide with anhydride is much greater than that of water with anhydride. From the relative concentrations of the two substances in the above solutions it might be expected that if the rates were nearly equal, only a little over 3 per cent of the anhydride would have reacted with the hydrogen peroxide. The fact that about the same per cent was obtained in the three experiments shows that the acetic acid has little influence upon the relative rates. An excess of hydrogen peroxide was present in each experiment. In the third only a little over 20 per cent of the hydrogen peroxide was used, and in the others much less. The secondary reaction of anhydride upon peracid would only tend to destroy the anhydride, and decrease the yield of peracid, as the active oxygen remains the same after this reaction.

A much better yield of peracid may be obtained by using a stronger solution of hydrogen peroxide, easily obtained by concentrating in a vacuum.

Twenty cc. of a solution of hydrogen peroxide containing 104 grams per liter were added to 6.1 grams of anhydride, and the mixture shaken and kept cool until the anhydride had gone into solution. It was then allowed to stand in a vessel of water for twenty-four hours. At the end of this time hydrolysis was complete, and the solution contained about 2 grams of peracid, about 45 per cent of the theoretical yield.

Anhydrides of Dibasic Acids.

Succinic Peroxide Acid, $\begin{matrix} CH_2COOH \\ | \\ CH_2COO \\ \quad\quad | \\ CH_2COO \\ | \\ CH_2COOH \end{matrix}$.—When a 3 per cent solution of hydrogen peroxide is saturated with succinic anhydride, the oxidizing power of the solution rapidly changes, as can be noted by its effect on potassium iodide. The products of the reaction remain dissolved, however, as there is no precipitation from the solution. If a stronger solution of hydrogen peroxide be employed and excess of anhydride be added, and the mixture shaken, so as to keep the solution saturated with the anhydride, a precipitation soon occurs. The anhydride used was in the form of broken pieces of a solid product, and after agitation it quickly settled to the bottom of the vessel. The precipitate consists of very fine crystals, and remains suspended in the liquid. After a considerable quantity had formed it was filtered, washed several times with water, dried quickly by packing tightly on a porous plate, then pulverized and allowed to remain in a vacuum for several hours. For analysis it was recrystallized from acetone. The active oxygen was estimated by dissolving the substance in a small amount of water, adding an excess of potassium iodide, and titrating at once with standard thiosulphate.

0.2383 gram substance gave 0.3563 gram CO_2 and 0.0871 gram H_2O.

0.1232 gram substance required 20.82 cc. N/20 thiosulphate.

	Calculated for $C_8H_{10}O_8$.	Found.
C	41.00	40.78
H	4.31	4.10
O (Active)	6.84	6.78

The amount of succinic acid present in the substance after complete hydrolysis and removal of active oxygen was determined and found to agree with the theoretical.

The substance was covered with about 20 parts of water in a test-tube, a pinch of platinum black added, and allowed to stand for a week. The succinic acid formed was then estimated by titrating with N/10 potassium hydroxide.

0.1954 gram substance required 33.25 cc. N/10 KOH.

Calculated, 33.40 cc.

0.1290 gram substance required 22 cc. N/10 KOH.

Calculated, 22.05 cc.

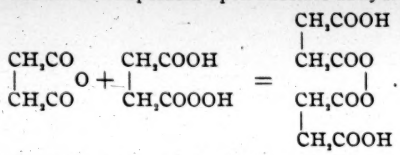
The substance is moderately soluble in water, alcohol, acetone, and acetic ether; sparingly in ether; insoluble in chloroform, benzene, and ligroin. It is colorless and, when pure, odorless. The crystals are flat plates, generally very irregular. The substance begins to soften at 115° and is completely melted at 128° with decomposition. When brought into a flame it explodes; it does not explode on percussion or friction. When openly exposed to the air it slowly deteriorates, but when well stoppered no deterioration could be detected after several months.

Assuming the action of succinic anhydride upon hydrogen peroxide to be similar to that of acetic anhydride, the first step is the formation of succinic monoperacid,

$$\begin{matrix} CH_2CO \\ | \\ CH_2CO \end{matrix} O + \begin{matrix} H \\ | \\ OOH \end{matrix} = \begin{matrix} CH_2COOH \\ | \\ CH_2COOOH \end{matrix}.$$

At the same time a certain amount of anhydride undergoes ordinary hydrolysis with water with the formation of succinic acid. The strength of the hydrogen peroxide solution employed determines the proportion in which the anhydride enters into each of these reactions. Succinic monoperacid is very soluble in water and does not separate from the solution.

The second step in the formation of the peroxide acid is the action of succinic monoperacid upon succinic anhydride :



The best yield of the peroxide acid is obtained by employing a 7.5 to 8 per cent solution of hydrogen peroxide.

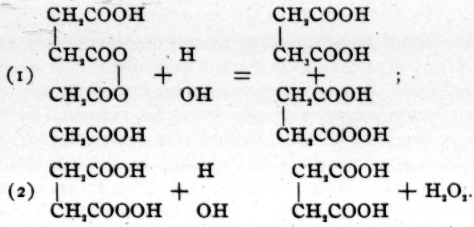
Ten grams of ordinary crystalline succinic anhydride were added to 25 cc. of 7.5 per cent hydrogen peroxide and the mixture shaken. The temperature gradually rose, but was kept below 30°. At the end of thirty-five minutes there was no further rise in temperature, indicating that all anhydride had been dissolved. The product was then filtered and washed several times with small portions of water. It was then packed tightly on a porous plate, placed in a warm place, and after an hour was perfectly dry. An analysis showed the substance to be pure. Yield, 7.5 grams.

When excess of the peroxide is added to water and shaken the amount dissolved gradually increases. This increase is due to the hydrolysis of the dissolved peroxide, which takes place according to the laws previously developed.[1] The rate of the reaction is much greater than that with any peroxide previously studied.

An excess of finely pulverized peroxide was continuously shaken with water at about 24°. At intervals of five, ten, fifteen, and twenty-five minutes a small portion of the mixture was filtered and the amount of peroxide dissolved was determined. At the end of five minutes the solution contained 19.8 grams per liter; at the end of ten minutes, 24.5 grams per liter; at the end of fifteen minutes, 28.4 grams per liter; and at the end of twenty-five minutes, 35.8 grams per liter. At this rate of hydrolysis, the original solubility may be placed approximately at 15 grams per liter. At the end of fifteen minutes the original solubility is almost doubled.

[1] *Loc. cit.*

A large excess of peroxide was added to water in a beaker and kept stirred continuously for several hours. The rate of hydrolysis as indicated by the active oxygen content of the solution was found to decrease as the solution became stronger. At the end of one-half hour hydrogen peroxide could easily be detected in the solution by means of the titanic or chromic acid tests. After six hours an appreciable portion of the active oxygen of the solution (over 0.5 per cent) was present as hydrogen peroxide. By this means it was possible to obtain a very strong solution of the products of hydrolysis. The substance hydrolyzes according to the following equations. The second change is much slower than the first:



Succinic peroxide acid presents a striking difference from other bodies of the peroxide type in the behavior af the unhydrolyzed substance toward potassium iodide. The action of the peroxide, as well as its hydrolytic product upon potassium iodide, is almost immediate, so that the substances cannot be distinguished from each other as could the peroxides and peracids of monobasic acids. When an excess of potassium iodide is added to a fresh saturated solution of the peroxide acid, or to the same solution after standing an hour, and which would, therefore, be mostly hydrolyzed, the calculated amount of iodine is liberated in the short time required to make the titration with standard thiosulphate. If the solution is very dilute, a minute or two is required before the liberation of iodine is complete. It was not possible, therefore, to study the hydrolysis of the peroxide acid in dilute solution. The change into hydrogen peroxide could be fol-

lowed, however, by comparing the immediate liberation of iodine with the total.

The following figures indicate the gradual formation of hydrogen peroxide: (1) in a 1 to 1000 solution, and (2) in a 1 to 100 solution:

Time in days.	(1) Per cent of active oxygen as H_2O_2.	(2) Per cent of active oxygen as H_2O_2.
1	7.3	5.3
2	14.0	8.3
7	41.0	40.0

The active oxygen content of the weaker solution had not appreciably decreased at the end of one week. In the stronger solution there was a decrease of only 1.5 per cent.

In addition to its action on potassium iodide the following are interesting properties, possessed by a solution of succinic peroxide acid. A small amount of manganous salt added to the solution soon produces the deep rose-red color of permanganic acid. The reaction is an extremely delicate test for traces of manganese. The coloration is prevented by the presence of considerable mineral acid. An excess of manganese salt gives, of course, manganese dioxide. The red solution of cobaltous salt is changed to an emerald-green, owing probably to the formation of a cobaltic salt; the solution slowly evolves oxygen. The addition of sodium acetate to the solution produces a precipitate, probably a higher oxide of cobalt. The green solution of a nickelous salt is soon changed to a purple, which is probably due to the formation of a nickelic salt. The latter seems to be unstable, however, as the solution evolves oxygen and in the course of a few hours the purple color disappears. The addition of sodium acetate to the purple solution causes immediate change to green with evolution of oxygen.

Finely divided manganese dioxide appears to have no catalytic action upon a solution of the peroxide acid, but is oxidized in part to permanganic acid. Lead dioxide has no catalytic action, but platinum black has a slight action. The solution has no effect upon chromic acid, titanic acid, or

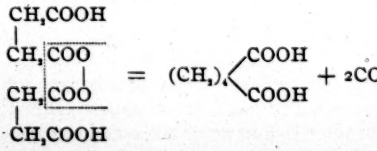
potassium permanganate, until it has stood an hour or more and hydrogen peroxide has been formed.

As already stated, succinic peroxide acid, like all peroxides, decomposes when heated. The decomposition was studied by adding the substance to xylene, which was heated to its boiling-point. Carbon dioxide was evolved, the amount being a little less than 1 molecule per molecule of peroxide. Only a trace, if any, of oxygen or hydrocarbons was evolved. On cooling the xylene a crystalline product separated, which was about 50 per cent of the original weight of substance. This product consisted chiefly of succinic anhydride, which was removed by digesting with chloroform on the water-bath. The residue was distilled, whereupon water, succinic acid, and anhydride passed over. The residue from this distillation consisted chiefly of adipic acid, which was recrystallized from water and identified by its melting-point.

0.1204 gram substance required 16.45 cc. N/10 KOH.

Calculated for adipic acid, 16.45 cc.

From the original xylol solution there was obtained, after removal of the solvent, a gummy residue, which dissolved completely in sodium carbonate. It was not identified. A small portion of the substance, therefore, decomposes as follows:



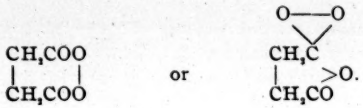
The major portion, however, decomposes to yield succinic anhydride, and the gummy acid substance already mentioned.

Vanino and Thiele[1] have described a substance obtained by the action of succinyl chloride upon sodium peroxide hydrate, which they have called succinyl peroxide and to which they have assigned the formula $C_4H_4O_4$. Baeyer and Villiger[2] have pointed out that the insolubility of the substance in water

[1] Ber. d. chem. Ges., 29, 1724.

[2] *Ibid.*, 34, 762.

and in all other solvents renders improbable such a simple formula as the one assigned. We have prepared the substance according to the directions of Vanino and Thiele in order to determine the per cent of active oxygen. There is no way to purify the substance so that the crude product, well washed and dried, was used. This product may be an individual substance or it may be a mixture. The yield obtained was very small. If the substance is covered with a 20 per cent solution of acetic acid and potassium iodide, it gradually goes into solution after six or eight hours, with the liberation of iodine. The percentage of active oxygen, so estimated, was 10.5, a correction having been made for a blank. The percentage calculated for $C_4H_4O_4$ is 13.8. The substance is described in Richter's "Chemie der Kohlenstoff-Verbindungen" as having either the formula



There is certainly no ground at present for assigning any formula to the substance, even assuming that the product in question is homogeneous in composition.

Succinic Monoperacid, $\begin{matrix} CH_2COOH \\ | \\ CH_2COOOH \end{matrix}$.—Ten grams of succinic peroxide acid were covered with about 75 cc. water in a beaker and stirred continuously at a temperature of about 30°. At the end of three or four hours the entire amount had gone into solution. It was then removed to an evaporating-dish and allowed to remain in a vacuum over night with sulphuric acid. The dry residue consisted of about 45 per cent of succinic monoperacid. The monoperacid is more soluble in chloroform than succinic acid, and may be removed from the latter by digesting the mixture with chloroform at 50°, filtering, and cooling the solution. In this way the substance is obtained fairly pure. It may be recrystallized from a mixture of chloroform and ether, from which it separates in large

crystals on standing. The percentage of active oxygen contained by various samples which were recrystallized several times, varied from 10.5 to 11.3, while the theoretical is 11.9. This deficiency may have been due to the fact that when the substance is dissolved in water a decided evolution of oxygen is noticeable; it was necessary to dissolve in water to estimate the active oxygen. A sample recrystallized twice contained 11 per cent of active oxygen and when rapidly heated melted at 107° with decomposition.

0.1170 gram substance gave 0.1546 gram CO_2 and 0.0473 gram H_2O.

	Calculated for $C_4H_6O_5$.	Found.
C	35.81	36.03
H	4.52	4.53

The substance is much more soluble in water than succinic acid. The same relation exists between the solubilities of benzoic acid and peracid. It also dissolves freely in alcohol, acetone, and acetic ether. It is only moderately soluble in ether and sparingly in chloroform. It has very little, if any, odor and does not, in the least, remind one of hypochlorous acid, as do benzoic and acetic peracids. It gradually decomposes on standing, but is more stable than benzoic peracid. A sample consisting of a mixture of succinic acid and monoperacid was found on analysis to consist of 60 per cent of the latter. After standing for a week in a stoppered vessel the percentage of monoperacid was only 55.4.

When a strong aqueous solution of the substance (either pure or mixed with succinic acid) is saturated with succinic anhydride, a heavy precipitate of succinic peroxide acid soon appears; more quickly on cooling and scratching with a glass rod. When glutaric anhydride is dissolved in a strong solution of the monoperacid the mixed peroxide acid of succinic and glutaric acids is formed and on cooling separates from the solution. This substance will be described later.

The decomposition of succinic monoperacid is interesting. The mixture of acid and monoperacid was used for this study.

It was mixed with infusorial earth in order to moderate the action.

Three and five-tenths grams of the mixed acids containing 1.6 grams of monoperacid were mixed with 5 grams of infusorial earth and placed in a small flask connected with a carbon dioxide generator and a gasometer. The air in the flask was completely replaced by carbon dioxide and the flask was then slowly heated in an oil-bath, and the gas evolved was collected over water in the gasometer. The volume of gas evolved was about 350 cc. This consisted almost entirely of carbon dioxide, with only a trace of oxygen and a small amount (about 3 per cent) of a combustible gas. The amount of carbon dioxide obtained is a little in excess of 1 molecule from 1 molecule of the monoperacid.

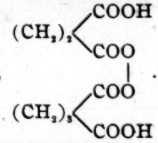
The experiment was repeated in order to determine the nature of the non-gaseous products. After the decomposition was completed the contents of the flask were distilled. Considerable water passed over at first and the temperature gradually rose to 140°. The distillate possessed the characteristic odor of acrylic acid. That it consisted in a large part of this substance was shown by treating it with concentrated hydriodic acid, whereupon β-iodopropionic acid crystallized from the solution. This was recrystallized from water and identified by its melting-point. The decomposition may be explained as follows:

$$(1)\quad \begin{matrix} CH_2COOH \\ | \\ CH_2\overline{COO}OH \end{matrix} = \begin{matrix} CH_2COOH \\ | \\ CH_2OH \end{matrix} + CO_2;$$

$$(2)\quad CH_2OHCH_2COOH = CH_2{=}CHCOOH + H_2O.$$

The substance first splits off carbon dioxide. The β-hydroxypropionic acid, which is probably formed as an intermediate product, then splits off water with the formation of acrylic acid. The decomposition probably takes place almost entirely in the manner indicated. Baeyer found that benzoic peracid decomposed with the formation of benzoic acid and oxygen. The results obtained with succinic monoperacid have suggested that possibly phenol is also formed

during the decomposition of benzoic peracid. This is made probable from the fact that benzoic peracid becomes colored on standing. Phthalic monoperacid, discovered and described by Baeyer, was found to yield salicylic acid on decomposition. This was identified by its color test with ferric chloride.

Succinic Glutaric Peroxide Acid,  .—Ten cc. of a solution of succinic monoperacid containing 1.47 grams of this substance and which was free from hydrogen peroxide was treated with 1.5 grams of glutaric anhydride. The latter substance was dissolved after shaking for a minute. The solution was kept cool under a tap and after about five minutes a crystalline precipitate appeared. After standing for five minutes longer the product was filtered, washed several times with small portions of water, and packed tightly on a porous plate. When dry, the substance was practically pure. Yield, 1.2 grams. For analysis it was recrystallized from a mixture of ether and acetic ether.

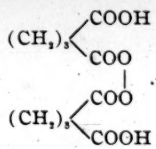
0.0825 gram substance required 13.25 cc. N/20 thiosulphate.

0.1473 gram substance gave 0.2344 gram CO_2 and 0.0650 gram H_2O.

	Calculated for $C_9H_{12}O_8$.	Found.
C	43.52	43.40
H	4.88	4.96
O (Active)	6.45	6.40

The substance begins to soften at 105° and melts at 107° with decomposition. It is quite soluble in alcohol, acetone, and acetic ether, and sparingly soluble in ether. The crystals are similar in appearance to those of succinic peroxide acid. When potassium iodide is added to a saturated solution of the substance, it must stand two or three minutes before the theoretical amount of iodine is liberated. In oxid-

izing action it is, therefore, less powerful than succinic peroxide acid.

Glutaric Peroxide Acid,  .—Three grams of glutaric anhydride were dissolved in 6 cc. of 8 per cent hydrogen peroxide. The solution was kept cool and the peroxide acid soon crystallized out. After twelve minutes it was filtered off, washed well with small portions of water, and dried on a porous plate. The dried substance was practically pure. Yield, 1.9 grams. For analysis it was crystallized from acetic ether.

0.0888 gram substance required 13.25 cc. N/20 thiosulphate.

0.1578 gram substance gave 0.2640 gram CO_2 and 0.0756 gram H_2O.

	Calculated for $C_{10}H_{14}O_8$.	Found.
C	45.77	45.61
H	5.39	5.37
O (Active)	6.10	5.97

The substance melts sharply at 108° with decomposition. It is quite soluble in alcohol, acetone, and acetic ether; moderately soluble in ether; and very sparingly in chloroform and benzene. The substance hydrolyzes in aqueous solution and the solubility and rate of hydrolysis were determined at 24° in the same manner as with succinic peroxide acid.

The amounts of peroxide acid contained in 1 liter of solution at intervals of five, ten, fifteen, and twenty-five minutes were 9.75, 10.75, 11.6, and 13.75 grams, respectively. At this rate of hydrolysis the original solubility may be placed approximately at 8.75 grams per liter.

The action of glutaric peroxide acid upon potassium iodide is markedly different from that of succinic peroxide acid. The action is very slow, like that of hydrogen peroxide. As

in the case of the latter substance, the time required for the complete liberation of iodine is greatly decreased by the addition of dilute sulphuric acid. Except in very dilute solution of peroxide the theoretical amount of iodine is liberated in fifteen minutes when excess of potassium iodide has been added.

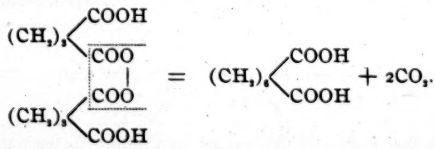
The decomposition of glutaric peroxide acid was studied in the same manner as that of the succinic compound.

Four and five-tenths grams of the substance were added in small portions to 15 cc. of boiling xylene. The non-volatile products of decomposition remained dissolved, but, on cooling, 0.6 gram of colorless crystals was deposited. This product was found to be almost pure suberic acid. The substance was purified by recrystallizing from water and melted at 140° (suberic acid 140°).

0.1156 gram substance required 13.45 N/10 KOH.

Calculated, 13.3 cc.

On distilling off the xylene from the filtrate previously mentioned, a fatty residue remained which was soluble in sodium carbonate. The decomposition takes place only to a certain extent as follows:



By the action of sodium hydroxide and hydrogen peroxide upon phthalic anhydride, Baeyer and Villiger[1] have isolated phthalic monoperacid, $C_6H_4\begin{cases}COOH\\COOOH\end{cases}$, and phthalic peroxide acid, $C_6H_4\begin{cases}CO.OO.OC\\COOH\ HOOC\end{cases}C_6H_4$.

These authors have offered no explanation of the reactions involved. If we consider that the addition of an alkali to a

[1] Ber. d. chem. Ges., 34, 762.

solution of hydrogen peroxide results in the formation of a salt of this substance, either MOOH or MOOM, then the reaction between such a solution and an anhydride may be looked upon as follows:

$$(1)\quad \begin{matrix}\mathrm{RCO}\\ \mathrm{RCO}\end{matrix}\!\!>\!\mathrm{O} + \begin{matrix}\mathrm{OM}\\ \mathrm{OM}\end{matrix} = \begin{matrix}\mathrm{RCOOM}\\ \mathrm{RCOOOM}\end{matrix},$$

and

$$(2)\quad \begin{matrix}\mathrm{RCO}\\ \mathrm{RCO}\end{matrix}\!\!>\!\mathrm{O} + \begin{matrix}\mathrm{M}\\ \mathrm{OO.OCR}\end{matrix} = \begin{matrix}\mathrm{RCOOM}\\ \mathrm{RCO.OO.OCR}\end{matrix}.$$

Such a view would explain all of the reactions which are known to take place between sodium peroxide, barium peroxide, etc., and acid anhydrides, chlorides, etc. This explanation is, however, not in accord with the views of Calvert,[1] who, after attacking from all sides the problem of the condition of hydrogen peroxide in alkaline solution, arrived at the conclusion that a compound of the type MO_3 is formed, M being a univalent metal. The work of Calvert has certainly shown that 1 molecule of alkali is capable of holding in combination more than 1 molecule of hydrogen peroxide. This behavior might be due to the formation of an addition-compound between hydrogen peroxide and its primary salt, such as $KHO_3.H_2O_2$. Schöne[2] has isolated compounds of this type by evaporating an alkaline solution of hydrogen peroxide in a vacuum. A compound[3] containing sodium acetate and hydrogen peroxide crystallizes out on adding sodium peroxide to acetic acid. Tanatar[4] has isolated compounds between other salts and hydrogen peroxide. Calvert showed that the solubility of potassium chlorate is greater in a solution of hydrogen peroxide than in water, and that its electric conductivity is less, although it would be expected to be greater, on account of the dielectric constant of hydrogen peroxide being greater than that of water. Jones and Carroll[5] further found that the depression of the freezing-point, brought

[1] Ztschr. phys. Chem., **38**, 513.
[2] Ann. Chem. (Liebig), **193**, 241.
[3] Tafel: Ber. d. chem. Ges., **27**, 816.
[4] Ztschr. anorg. Chem., **28**, 255.
[5] This JOURNAL, **28**, 284.

about by various salts in hydrogen peroxide solution, was less than that in water, and have pointed out the probability that compounds are formed between hydrogen peroxide and salts in solution. An unstable compound between the benzoylated hydrogen peroxide and its sodium salt has been observed by Baeyer and Villiger.[1] A number of weak acids are known to form compounds of this type, and we may even look at compounds containing water of crystallization in the same light. It is not known whether or not such compounds are completely dissociated in aqueous solution. The similarity between hydrogen peroxide and water which has been pointed out in this article makes it appear possible that water enters into combination with neutral salts dissolved in it. In this connection the results obtained by Calvert and by Jones and Carroll appear especially interesting.

The following may be summed up as the chief reactions which are known to take place when an anhydride is dissolved in an aqueous solution of hydrogen peroxide:

(1) Ordinary hydrolysis with water.

(2) Analogous reaction with hydrogen peroxide resulting in the formation of a peracid.

(3) Action of peracid on anhydride with the formation of an acid peroxide.

(4) Ordinary hydrolysis of peroxide with water.

(5) Action of hydrogen peroxide upon acid peroxide with the formation of 2 molecules of peracid and also with loss of oxygen, possibly due to the intermediary formation of a derivative of hydrogen trioxide.

(6) Slow hydrolysis of peracid to acid and hydrogen peroxide.

(7) Slow decomposition of both peracid and hydrogen peroxide with evolution of oxygen.

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ANN ARBOR, Feb. 13, 1904.

[1] Ber. d. chem. Ges., 33, 1569.

ON INULIN.

By Arthur L. Dean.

Numerous investigators have undertaken the study of inulin, some approaching their work with the aim and equipment of the botanist, some with those of the chemist. In general, the chemical investigations have contributed in a marked degree to the clearer understanding of the physiological rôle of inulin in plants. In the course of certain investigations on the physiological relations of inulin I have been led to study its behavior as a chemical compound with results which seem worth recording.

From the researches of the older workers the methods of preparation and the properties of inulin were fairly well established. In order to obtain preparations of inulin, the tissues containing it—almost always the underground parts of *Inula Helenium*, *Helianthus tuberosus*, or *Dahlia variabilis*—are finely divided, the juice squeezed out, the residue boiled with water with the addition of a little calcium carbonate to neutralize any acidity, and the fluid pressed out. The juice and the extract are united, purified with lead acetate, the excess of lead removed with hydrogen sulphide, and the filtrate from the lead sulphide neutralized with ammonia or calcium carbonate. The inulin in this solution, after concentration to a small volume, is removed either by freezing or by adding alcohol until the fluid contains about 60 per cent thereof. The product obtained in this manner is frequently somewhat discolored and sometimes contains traces of sugar. It may be purified by redissolving it in hot water, filtering through animal charcoal, and again precipitating by alcohol or freezing. The inulin obtained in this way is a white, odorless, tasteless solid, very sparingly soluble in cold water, readily soluble in hot water, and practically insoluble in cold alcohol of 60 per cent strength or over. It does not reduce Fehling's solution, but on short boiling with acids or by the action of the enzyme inulase this carbohydrate is hydrolyzed to levulose, which readily reduces Fehling's solution. The well-known Seliwanoff's reaction[1] is given brilliantly. Inulin is

[1] On boiling solutions of the ketones, or their polymers, with 18 per cent of hydrochloric acid and a little resorcinol, a brilliant cherry-red color is produced with the subsequent separation of a red precipitate.

optically active, turning the plane of polarized light to the left. The exact amount of its specific rotation has been variously given, but in general the figures have ranged from $[\alpha]_D = -33°$ to $-40°$.

As stated above, the ordinary sources of inulin are the fleshy underground organs of the elecampane, artichoke, and dahlia. Preparations have also been made from chicory and dandelion roots. On account of the fact that in pieces of these plant organs kept in alcohol, sphaerocrystals of inulin develop, this reaction has been used as a microchemical test for inulin. Using this method, various investigators have tested a considerable range of plant species for the presence of this carbohydrate. Foremost among these researches should be mentioned those of G. Kraus, who showed that besides the wide occurrence of inulin in reserve places—outside the seeds—in the *Compositæ*, it is also present in members of the *Campanulaceæ*, *Lobeliaceæ*, *Goodeniaceæ*, and *Stylideæ*.[1] Kraus also made preparations of inulin from several of these non-composites and established its similarity, if not its identity, with the inulin of the *Compositæ*. It was noted by Kraus that glycerol gave this microchemical test as well as, and in some respects better than, alcohol.

Numerous investigators have noted that inulin is accompanied in the *Compositæ* by one or more carbohydrates of somewhat similar nature. Like inulin, they yield levulose on hydrolysis and are more or less insoluble in cold water and alcohol. In general, these compounds stand in an intermediate relation between inulin on the one hand and levulose on the other; they show a lesser laevo-rotation than inulin and a greater solubility. This mixture of substances,—for there can be little doubt that it is a mixture,—has been studied under the various names of levulin, inuloïd, and synanthrose; but the contradictory nature of the results of these studies of the levulins leave us with a very hazy knowledge.

The study of the reserve carbohydrates of various other plants, especially members of the monocotyledonous class, has

[1] G. Kraus: Das Inulin-Vorkommen ausserhalb der Compositen. Bot. Zeit., 1877, 329.

shown that there are here carbohydrates of the same general type as inulin, *i. e.*, they are laevorotary polymers of levulose, more or less insoluble in cold water and alcohol. The following table, although not including all the substances which have been studied, gives some facts about a number of them:

Name.	Source.	$[\alpha]_D$.
Irisin	*Iris pseudacorus*	−50 to −54
Sinistrin	*Scilla maritima*	−44 to −48
Graminin	*Trisetum alpestre et al.*	−38.9
Phlein	*Phleum pratense et al.*	−48 to −49

In 1893 there appeared a considerable contribution to our knowledge of inulin and the levulins, embodied in a series of short papers by Tanret.[1] He made the fundamental criticism that all the previous preparations of inulin had been impure, having been contaminated with the levulins, and that therefore the properties of inulin as given by the older workers are incorrect. The new method of preparation, which is described in detail later in this paper, consisted in precipitating the inulin from its solutions as the barium compound by means of barium hydroxide. This barium compound, on account of its greater insolubility, was separated from the barium compounds of the levulins. The levulins, by a further application of the method, were separated from one another, purified, studied, and named. Thus there are, starting from inulin and going down in the series, pseudoinulin, inulenin, helianthenin, and synanthrin. The following table summarizes the more important of Tanret's results:

Aside from the facts outlined in the table, it is noteworthy that Tanret says that on the hydrolysis of inulin he obtained not levulose only, but a mixture of 1 part of dextrose and 12 parts of levulose. The plants experimented with were the artichoke, dahlia, and elecampane, the first named apparently furnishing the bulk of the material worked with.

At the end of Tanret's last paper the following method is given: "Ainsi, étant donné du suc de topinambur, on com-

[1] "Sur l'inuline et deux principes immédiats nouveaux, la pseudo-inuline et l'inulénine," Compt. rend., **116**, 514 (1893); Bull. Soc. Chim., [3], **9**, 200; "Sur l'inuline." *Ibid.*, [3], **9**, 227; "Sur les hydrates de carbone du Topinambur," *Ibid.*, [3], **9**, 622.

Name.	Form.	$[\alpha]_D$.	Solubility in water at 15° C.	Molecular weight	Formula.[1]
Inulin	Spheroids	—39.5	1 to 10,000	4827	$30(C_{12}H_{10}O_{10})5H_2O_2$
Pseudoinulin	"	—32.2	1 to 350–400	2538	$16(C_{12}H_{10}O_{10})H_2O_2$
Inulenin	Bunches of needles	—29.6	1 to 8	1645	$10(C_{12}H_{10}O_{10})2H_2O_2$
Helianthenin	" " "	—23.5	1 to 1	1924	$12(C_{12}H_{10}O_{10})3H_2O_2$
Synanthrin	Amorphous	Ca —17.0	In all degrees	1319	$8(C_{12}H_{10}O_{10})H_2O_2$

[1] It should be noted that these formulas are given by an old method whereby the values for carbon and oxygen are twice what they should be; thus the formula of inulin would be written by us as $30(C_6H_{10}O_5)5H_2O$.

mence par le déféquer à chaud par l'extrait de saturne, etc., puis on l'additionne d'un grand excès d'eau de baryte concentrée et on précipite par de l'alcool à 90° et en une seule fois tous les hydrates de carbone. On décompose le précipité par CO_2, on fait bouillir, on filtre, puis on évapore à siccité. Le résidu, traité par l'alcool à 84° bouillant, lui abandonne l'hélianthénine qui se dépose en partie après un repos suffisant, la liqueur n'en retenant que 1/300. Le résidu insoluble est alors traité par l'alcool à 70° bouillant qui enlève l'inulénine. Ce qui reste ne contient plus que la pseudo-inuline et l'inuline, qu'on sépare en les traitant par 10 parties d'alcool à 60° bouillant : la pseudo-inuline y passe et l'inuline reste indissoute.''[1] It is stated in the foot-note that inulenin is soluble in 9 parts of boiling 70 per cent alcohol, and insoluble in cold alcohol of that strength ; that pseudoinulin is soluble in 6 parts of boiling 60 per cent alcohol, and insoluble in cold ; and that inulin is insoluble in cold 60 per cent alcohol and requires 2,000 parts of that strength of boiling alcohol to dissolve it. Tanret adds that he proposes to trace by this method the history of the carbohydrates of the artichoke, but I have been unable to find that he has published anything dealing with these carbohydrates since the appearance of the article quoted from above.

EXPERIMENTAL DATA.

Five plants have served as the sources from which the preparations of inulin to be described have been obtained : *Dahlia variabilis*, *Inula Helenium*, *Helianthus tuberosus*, *Lappa minor*, and a mixture of *Solidago* species. Of these, the first three have long been used as sources of inulin, but, so far as I am aware, no preparations of inulin have been made from the roots of the burdock or from those of the goldenrods. The inulin has been obtained by two methods, the method of the older investigators as described above and by what we will call the second method of Tanret, given in the quotation from the Bulletin of the Chemical Society of Paris.

The fact that the common burdock has long, rather fleshy

[1] Bull. soc. chim., [3], 9, 629 (1893).

roots which persist until the time of flowering, suggested the idea that these roots might contain inulin. Accordingly, a number of the roots were dug in October and tested as follows: The roots were washed, grated to a fine pulp, and the mass, together with a little calcium carbonate, was treated with water for about thirty minutes on a boiling water-bath. The fluid was then expressed, lead acetate added in slight excess, the excess of lead removed from the filtrate with hydrogen sulphide, the resulting solution neutralized with ammonia, the fluid concentrated on the water-bath, and treated with an excess of alcohol. After standing over night the precipitate was filtered off, dissolved in water, and the solution run through washed animal charcoal. To this clear, colorless liquid alcohol was added to the strength of 61 per cent. After standing, the precipitate was filtered on a Büchner funnel, washed by being whipped up successively in 60 per cent alcohol, absolute alcohol, and ether, and finally dried. The resulting product was perfectly white, consisted of small spheroids, free from proteid, sparingly soluble in cold water, but readily soluble in hot water. It did not reduce Fehling's solution until after boiling with dilute acids. Seliwanoff's reaction was readily obtained. Dried to constant weight and examined by the polariscope, it was found to be laevorotary, $[\alpha]_D$ being equal to $-36°.36$. From these properties it is evident that we are dealing with inulin.

The fibrous roots of the goldenrods present a marked contrast to the fleshy underground parts of the other *Compositæ* which have been examined. Some of these roots, gathered in October and cleaned from gravel as far as possible, were put through the process detailed above and yielded a white preparation consisting of spheroids, giving Seliwanoff's reaction, and reducing Fehling's solution only after boiling with acids. The first preparation, made from the roots of plants still in flower, was noticeably more soluble in cold water than are the ordinary preparations of inulin. A second preparation, made from the roots of plants, the aerial parts of which were already dead, was markedly more insoluble and could not be distinguished by its solubility from the ordinary run

of inulin. Examined by the polariscope, this last preparation gave a specific rotation of $[\alpha]_D = -35°.7$. From this evidence it seems safe to conclude that the roots of the goldenrods contain inulin.

I have examined the aerial parts of the inulin-containing plants in a number of instances, and in only one case has evidence of the presence of inulin or of the levulins been obtained. Thus the leaves and stems of the dahlia, the leaves and half-matured seed-heads of the artichoke, the leaves of the goldenrods, and the leaves and petioles of the burdock, all gave negative results. From the stems of the artichoke, however, a preparation was obtained which had the characteristics of inulin except that, like the first preparation from the roots of *Solidago* mentioned above, it was more soluble than inulin in cold water, resembling in this respect a preparation made three days before (October 3rd) from the tubers of an artichoke plant growing near by.

Inasmuch as the older method of preparing inulin gave preparations of inulin possessing differing properties, it seemed advisable to try the method of Tanret to attempt to obtain constant results thereby. The first method given by Tanret, which I have not yet described, was worked through very carefully, as detailed below.

Artichoke tubers gathered partly October 3rd and partly October 17th were ground together, and extracted twice with boiling water with the addition of calcium carbonate. The strained extract was treated with an excess of neutral lead acetate, filtered clear, and sulphuric acid added in very slight excess to remove the excess of lead. The filtrate from the lead sulphate was treated with cold saturated barium hydroxide solution until no more precipitate fell, then 95 per cent alcohol was added until it made one-sixth of the volume of the mixture, then more saturated barium hydroxide solution containing 16 per cent of alcohol until the precipitation was complete. The precipitate was filtered on a Büchner funnel, washed with 16 per cent alcohol saturated with barium hydroxide, then removed from the filter, suspended in water, and decomposed with carbon dioxide, the mixture being

warmed during the process to facilitate the reaction. The filtrate from the barium carbonate was cooled and a saturated solution of barium hydroxide added to complete precipitation. This "precipitate (A)" was filtered off and successive small amounts of alcohol added to the filtrate until no more precipitate was obtained. The second precipitate, after removal by filtration, was decomposed with carbon dioxide, the barium carbonate filtered off, and the clear filtrate saved as the "liquid (B)." The "precipitate (A)" was rubbed up in water, decomposed with carbon dioxide, and the filtrate precipitated by barium hydroxide. The filtrate from this new "precipitate (A)" was treated with alcohol and the resulting precipitate decomposed with carbon dioxide, yielding an increment to the "liquid (B)." This process of fractionating (A) was repeated three more times, (A) becoming constantly smaller and the "liquid (B)" constantly increasing. The last time the "precipitate (A)" was smaller than the precipitate resulting from the addition of alcohol to the filtrate from it. Even this very small fraction was not all precipitable by saturated barium hydroxide solution, which is the test by which we are to know that inulin is finally free from admixture with the levulins.

In this experiment, therefore, six successive fractionings of the barium compounds of inulin and the levulins failed to give a separation. No better results followed the attempt to continue Tanret's process on "the liquid (B)" and obtain therefrom pseudoinulin and inulenin.

This rather discouraging result led to a trial of Tanret's second method as given in the quotation from his last paper. Preparations of inulin from all five of the plants named above were made by this method. With one exception the amounts of the various levulins were too small to admit of making polariscopic examinations of them. Their forms, as seen under the microscope, were noted and Fehling's and Seliwanoff's tests were applied. In all cases the precipitates occurring when, according to Tanret, helianthenin and inulenin should have come down, were made up of minute, needle-shaped crystals, generally loosely aggregated into balls. No

characteristic difference of form between the two was noted. The precipitates corresponding to pseudoinulin were made up of irregularly sized spheroids and showed a tendency to form a coherent layer at the bottom of the alcohol from which they had separated. The inulin residues remaining after the various extractions with alcohol were more or less discolored and sometimes contained a little insoluble material. They were always dissolved in hot water, filtered, and precipitated by adding alcohol to the strength of 60 per cent. The results of this systematic use of the second Tanret method are given below.

Lappa minor.—Burdock roots, dug November 21st, were cleaned, grated, and put through the second Tanret method. The inulin residue from the alcoholic extractions was so discolored that its solution was run through charcoal before precipitating with alcohol. The precipitate was filtered off and washed with absolute alcohol and ether. Dried to constant weight it showed a specific rotation of $[\alpha]_D = -40°.5$. The precipitates of the levulins were slight.

Inula Helenium.—Roots of the elecampane were dug October 11th. After being comminuted, the material was spread in a thin layer and allowed to dry at laboratory temperature. When air-dry, the tissues were ground to a fine powder and kept in that condition. Tanret's process was applied to an extract obtained by boiling this *Inula* powder with water and a little calcium carbonate. The substance corresponding to the synanthrin of Tanret weighed, air-dry, 3.9 grams. There was no helianthenin precipitate, the inulenin weighed 0.3 gram, the pseudoinulin 0.45 gram, and the inulin, dried to constant weight, 38.6 grams. The specific rotation was equal to $[\alpha]_D = -37°.2$. The preparation contained 0.14 per cent of ash.

Solidago.—The roots of a number of species of *Solidago* were gathered November 15th, washed, and immediately examined for inulin. The precipitates of the levulins were either entirely lacking or very slight. The specific rotation of the inulin obtained was $[\alpha]_D = -37°.2$, which is 1°.5 higher

than the rotation of the inulin obtained by the other method from roots gathered October 24th. The ash of the goldenrod inulin amounted to 0.21 per cent.

Helianthus tuberosus.–Artichoke tubers, dug November 18th, were ground up the same day and an inulin preparation made in the same way as the others. In this case a good yield of helianthenin, 2.1 grams, was obtained. This preparation, which was composed of balls of fine needles, was filtered off, washed with 95 per cent alcohol, absolute alcohol, and ether, and, after drying, examined by the polariscope. It was found to have a specific rotation of $[\alpha]_D = -21°.97$, which is seen to lie between those of Tanret's helianthenin and his synanthrin. Accordingly, this preparation was fractionated to obtain pure helianthenin if possible. Its solution, which was slightly turbid, was shaken up with alumina cream, filtered perfectly clear, and absolute alcohol added to incipient precipitation. After standing over night, the precipitate which had formed was collected on a hardened filter, washed with absolute alcohol and ether, dried, and its specific rotation determined. This was found to be $[\alpha]_D = -26°.06$, which lies midway between helianthenin and inulenin. The preparation of inulin from the artichoke had an ash content of 0.17 per cent and gave a specific rotation of $[\alpha]_D = -33°.4$.

Dahlia variabilis. — Growing plants of the dahlia were rooted up October 29th, and the tuberous roots, after being kept in the laboratory several days, were put through the second Tanret process for inulin. Small quantities of the levulins were obtained and a preparation of inulin having 0.28 per cent of ash and a specific rotation of $[\alpha]_D = -33°.02$. Assuming the correctness of the solubilities given by Tanret and also the specific rotation of inulin given by him, it is remarkable that one should obtain inulin preparations having as low a rotation as those of the inulin of the artichoke and dahlia just described. To further test this point, the inulin obtained from the dahlia was treated with alcohol as follows: Exactly 3 grams of dry inulin were weighed out and boiled twice with 30 cc. of 60 per cent alcohol, made from absolute alcohol

by dilution, and the residue was washed on the filter with boiling 60 per cent alcohol. This treatment surely ought to have removed all the levulins if their solubilities are as Tanret gives them. The total alcoholic filtrate and washings were collected in a tared beaker, dried first on the water-bath and finally in the drying-oven, until the residue lost no more weight. This preparation weighed 0.5984 gram and had a specific rotation of $[\alpha]_D = -26°.1$. From this it appears that the undissolved residue weighed 2.4016 grams and had a rotation of $[\alpha]_D = -34°.7$.

Inasmuch as it was thus shown that the second method of Tanret could not be relied upon to give inulin preparations which would always show a specific rotation of 39° to 40°, it was deemed worth while to compare the yields and specific rotations of inulin made by the two methods: that of the older workers which we may call Dragendorff's method and Tanret's second method. Accordingly, some dahlia tubers, which had been taken up in the fall and kept in loam in a cool cellar, were examined in January as follows: The juice of the ground tubers was expressed, the tissue residue boiled in water with a little calcium carbonate, and the fluid expressed. The united extracts were treated with lead acetate n excess and the precipitate removed by filtration. Two portions of this filtrate, of 965 cc. each, were separately worked up for inulin, one by each method. By the Dragendorff method the extract, after removal of the lead with hydrogen sulphide, was percolated through charcoal, concentrated to 140 cc., and precipitated by the addition of absolute alcohol to 60 per cent. The other portion of the extract was treated with a slight excess of sulphuric acid for the removal of the lead, but, on account of the very slight excess of lead acetate, the precipitate of lead sulphate was too small and fine to be removed by filtration. The fluid was accordingly treated with an excess of cold saturated barium hydroxide solution and then methyl alcohol added until it made about 30 per cent of the whole. The copious precipitate was collected in a Büchner funnel, carefully transferred to a beaker, rubbed up with water, and carbon dioxide run in for about

one-half hour. Then the mixture was warmed on a water-bath, carbon dioxide being passed in during the warming. The decomposition of the barium inulinate was continued until complete, as shown by the reaction of the fluid and the nature of the precipitate. The solution was boiled, filtered, and the filtrate dried on the water-bath. The residue, which weighed 25 grams (it probably contained much moisture still), was ground to a fine powder and extracted with 250 cc. of 84 per cent alcohol, of 70 per cent alcohol, and of 60 per cent alcohol, respectively, the filtrations being carried out in a hot-water funnel to prevent error by the cooling of the alcohol. The residue was dissolved in 140 cc. of water and precipitated by adding alcohol to 60 per cent. The processes were carried out with great care at every step to avoid losses, although the nature of the processes, especially the Tanret method, precludes very exact quantitative manipulations. Both inulin precipitates were filtered on hardened papers, washed with the same strengths of alcohol, and dried. The inulin by the Dragendorff method was slightly discolored on account of the inadequacy of the charcoal filtration. Dried to constant weight it weighed 22.5 grams and had a specific rotation of $[\alpha]_D = -34°.2$. The inulin by the Tanret method was whiter, weighed 14 grams, and had a rotation of $[\alpha]_D = -36°.8$.

It is worth noticing that the inulin prepared by the Tanret method from *Dahlia*, when the plants were still in vigorous growth, showed a specific rotatory power of $[\alpha]_D = -33°.02$.

It has been observed in many cases that by solution and reprecipitation of inulin preparations the specific rotation rises. Assuming that if such a procedure were repeated until a constant rotation was obtained one would then have pure inulin, the properties of which might be determined, I carried out the experiments to be detailed.

I. Preparation A; from Lappa minor.—A1. Prepared from burdock by Dragendorff's method. $[\alpha]_D = -35°.3$.

A2. A1 dissolved, precipitated by alcohol to 60 per cent, washed in cold 60 per cent, and boiled in 60 per cent alcohol. $[\alpha]_D = -37°.6$.

A3. A2 treated as last. $[\alpha]_D = -39°.6$.

A4. A3 treated as last. $[\alpha]_D = -37°.8$.

II. Preparation B; from Lappa minor.—B1. Prepared from burdock by second Tanret method. $[\alpha]_D = -40°.5$.

B2. B1 dissolved in water, precipitated by alcohol to 60 per cent, boiled in 60 per cent alcohol, washed in absolute alcohol and ether. $[\alpha]_D = -38°.8$.

III. Preparation C; from Dahlia variabilis.—C1. Prepared from dahlias by Dragendorff's method. $[\alpha]_D = -33°.4$.

C2. C1 dissolved and precipitated by the addition of alcohol to 60 per cent. $[\alpha]_D = -36°.4$.

C3. C2 dissolved and precipitated by alcohol to 60 per cent, dissolved and precipitated as before, boiled in 60 per cent alcohol, and washed with absolute alcohol and ether. $[\alpha]_D = -37°.8$.

C4. C3 dissolved, precipitated with alcohol to 60 per cent, boiled in 60 per cent alcohol. $[\alpha]_D = -40°.1$.

C5. C4 treated as last. $[\alpha]_D = -36°.2$.

IV.—In this experiment, instead of subjecting the inulin to be polarized to the long dryings necessary to get it to constant weight, the main part of the preparation was examined air-dry and a small sample removed and a moisture determination made on it. The results were then calculated for moisture-free substance. Two preparations, one from dahlias and one from burdocks, were run along side by side. The purifications, which were the same at every step and upon both samples, consisted of solution in water, precipitation by alcohol added to 60 per cent, boiling in 60 per cent alcohol, washing in hot 60 per cent alcohol, cold 95 per cent and absolute alcohol, and finally with ether. The ether was entirely removed by drying below 100°.

D1. From burdock, Dragendorff's method. $[\alpha]_D = -37°.2$.

E1. From dahlia, Dragendorff's method. $[\alpha]_D = -36°.6$.

D2. From D1 as described above. $[\alpha]_D = -38°.8$.

E2. From E1 as described above. $[\alpha]_D = -37°.1$.

D3. From D2 as described above. $[\alpha]_D = -34^\circ.7$.
E3. From E2 as described above. $[\alpha]_D = -34^\circ.9$.

Preparations D3 and E3 were kept for three months tightly stoppered in a desiccator over sulphuric acid before they were examined in the polariscope.

Judging by the results of these experiments it seems evident that inulin preparations cannot be obtained with a specific rotation much greater than —40°. Inulin in this condition appears to be unstable, at least its rotatory power decreases on solution and reprecipitation.

Conclusions.

It appears from the investigations of others and from the experimental evidence given above that we are justified in drawing the following conclusions:

1. Inulin obtained from the underground storage organs of *Dahlia variabilis*, *Helianthus tuberosus*, *Lappa minor*, *Inula Helenium*, and *Solidago* shows no essential differences and may be looked upon as the same.

2. Inulin is accompanied in these places by levulins, resembling inulin in composition, but differing from it in possessing a greater degree of solubility and a lower specific rotation.

3. The line of division between inulin and the levulins is apparently a very difficult one to draw; the physiological significance of such a division is somewhat problematical.

4. The first method devised by Tanret is an extremely tedious process and of somewhat doubtful value for general use. The second method, although rather long, is readily enough applied, but apparently involves some loss of material and does not yield preparations having the properties of inulin as given by the author of the process.

5. Tanret claims to have isolated and determined the properties of the various levulins, but the actual laboratory experience with his methods and the products obtained thereby force one to be somewhat skeptical about the results given in Tanret's papers.

6. The results obtained in the attempts to get pure inulin, using its specific rotation as a criterion of purity, are very puzzling; they may, however, be of value in helping us to form an idea of the nature of inulin. In this connection the results of attempts to determine the molecular weight of inulin are of interest. Tanret gives to inulin a molecular weight of 4827; Brown and Morris[1] found in two trials 2159 and 2209; Ekstrand and Mauzelius[2] were unable to obtain constant results on an inulin having a specific rotation of $[\alpha]_D = -35°.39$, but obtained lowerings of the freezing-point corresponding to molecular weights of from 796 to 4028. In the only determination which I have made, the depression of the freezing-point indicated a molecular weight of 2329, but when more inulin was added to the solution and the freezing-point again determined it was found to be the same as before, a very confusing and contradictory result; the inulin used had a specific rotation of $[\alpha]_D = -38°.6$.

There must be some explanation for the anomalous behavior of inulin as shown by the various data given above. Perhaps we do not know enough about it to form an intelligent hypothesis, but the following conception may be helpful: The living cells of the storage organs, in polymerizing the levulose brought to them, build it up into compounds of the percentage formula $C_6H_{10}O_5$, or perhaps $6(C_6H_{10}O_5)H_2O$, perhaps both. The compounds actually formed are made up of a variable number of these radicals in loose combination. In these substances, either when within the cells or when outside of them, the great looseness of the combinations of radicals allows ready changes of size and arrangement in the molecular aggregates, rearrangements which condition small differences of properties. Thus it is conceivable that the levulins of greater solubility are made up of a smaller number of molecular nuclei in the aggregates; and that inulin, with the largest molecules, highest rotatory power, and least solubility, stands at the head of the series. Inulin itself is

[1] "Molecular weights of the carbohydrates," J. Chem. Soc. (London), **40**, 462 (1889).

[2] "Moleculargrösse einiger dem Inulin verwandter Kohlenhydrate," Chem. Ztg., **13**, 1302, 1337 (1889).

apparently not a single, well-defined compound, but is the name of a variety and mixture of molecular complexes, which, on account of the narrow range of differences, have been regarded as a single substance. There is a suggestion in the experimental evidence that the solubility and specific rotation of inulin do not always vary together.

May we not, in a purely empirical way, call the carbohydrate, or carbohydrate mixture, which is readily precipitated in cold alcohol of 60 per cent strength, and has a specific rotation of $[\alpha]_D = -33^\circ$ to -40° inulin; and the undetermined mixture of lower rotatory power and greater solubility, the levulin mixture?

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A RAPID METHOD FOR THE DETERMINATION OF TOTAL SULPHUR IN IRON BY EVOLUTION.

BY S. S. KNIGHT.

The recent modification of the method for determining sulphur in iron, presented by Walters & Miller, of Pittsburg, Penna., had as its principal disadvantages the extraordinarily long time, which they claim would be at least an hour, under the most favorable circumstances, to complete a sulphur determination and also the expensive and unusual apparatus for roasting samples in a current of reducing gases.

In commercial laboratories which are not equipped with this apparatus the recent modification of this roasting process has consisted in roasting the weighed sample for a period of one hour at a slowly increasing temperature. The culmination of this annealing process was the highest heat obtainable before a blast-lamp, which was continued for at least fifteen minutes. The sample thus roasted was treated as heretofore by the evolution process.

In the laboratory of the Birmingham Pipe and Casting Company, the writer has been able to get results which check very closely with those obtained by the above-described

method, and also with those obtained by the barium chloride gravimetric method, by the following process:

The weighed sample, which in our case consisted of 2 grams, was mixed with 1 gram of the purest obtainable iron dust by hydrogen, and in which the sulphur content had been previously determined. This mixed sample is then placed in a small porcelain crucible and 1 gram more of the iron by hydrogen is sprinkled over the top so as to form a continuous covering. On top of this is placed a small disk of quantitative filter-paper, the lid is then placed on the crucible and this is placed on the triangle over the blast-lamp. For ten minutes the highest heat obtainable with the blast-lamp is used in roasting this mixture, at the expiration of which time it is allowed to partially cool, and the contents of the crucible are then placed in the ordinary evolution-flask and treated with hydrochloric acid, while the evolved gases are washed in any of the common forms of absorption bulbs. The absorbent liquid in our case has been an ammoniacal solution of cadmium chloride which was afterwards titrated with the iodine solution of known strength. The results obtained by this method are exactly those given by standard gravimetric methods and also the same as those obtained by Walters & Miller's method, while the time consumed is something less than one-half hour from the time the sample arrives in the laboratory.

It is believed by the writer that the advantage of this modification will be readily appreciated by chemists in charge of commercial laboratories.

BIRMINGHAM, ALA., Feb. 16, 1904.

REPORT.

Observations upon the Boiling-points of some Organic Liquias: A Method of Determining the Molecular Weights of Pure Liquids and Solids.

In an article under the above title, published in the "Annales Scientifiques de l'Université de Jassy" (March, 1901), G. G. Longinescu has pointed out that a simple relation exists between the boiling-points of organic liquids, their densities,

and the number of atoms in their molecules. Reviewing the work of Kopp, he shows that the boiling-points are dependent upon the number of atoms in the molecule and the number of molecules in unit volume. Schroeder has further shown that the boiling-point depends upon the arrangement of the molecules among themselves, and upon the grouping of the atoms in the molecule. A study of the relation between the molecular weights, densities, and boiling-points of various organic liquids has led the author to the conclusion that the ratio between their boiling-points is equal to the ratio between their densities, when this latter is multiplied by the square-root of the ratio between the number of atoms in the molecules of the two substances. This relation is expressed in the equation $\frac{T}{T'} = \frac{D}{D'}\sqrt{\frac{n}{n'}}$, where T and T' are the absolute boiling temperatures of the two liquids. D and D' their densities at 0°, and n and n' the number of atoms in their molecules.

From this equation it follows that if the number of atoms in the molecules of two substances is the same, the boiling-points are directly proportional to their densities, a fact which he shows to hold for a long list of isomeric substances. This proportionality may also be deduced from Van der Waals' equation for "change of state."

On applying this fundamental equation to a large number of compounds, Longinescu found it to hold very closely, while where the relation did not seem to exist, previous work had shown the molecules to be associated to a considerable extent. This led him to apply the equation to the determination of the degree of association of liquids and solids.[1] By a simple transformation Equation I. becomes

$$\frac{T}{D\sqrt{n}} = \frac{T'}{D'\sqrt{n'}} = \text{constant or } n = \left(\frac{T}{C \times D}\right)^2.$$

Taking some liquids that had been shown by other methods not to be associated he calculated this constant in a number of cases, and found it to be 100.

For associated liquids a different value was obtained, the maximum value (215) being found for water. The boiling-point and density of a liquid being known, all the data are then at hand for calculating the number of atoms in the molecule.

To test the equation $n = \left(\frac{T}{C \times D}\right)^2$, it was applied to over

[1] J. Chim. Phys., Oct., 1903.

125 non-associated liquids and gave in no case a difference of more than 2 atoms between the number as calculated and as given in the simplest chemical formula. It was further applied to liquids whose association had been determined by Ramsay, Vernon, and others, and gave results agreeing with theirs in a striking manner. Thus, the association of methyl alcohol was found to be 3.1, ethyl alcohol 2.2, propyl alcohol 1.7, acetone 1.6, while Ramsay, by his method, found for the corresponding substances 3.4, 2.7, 2.2, and 1.5.

By this method the association of formic acid was found to be 1.8, acetonitrile 3.1, aldehyde 2, nitroethane 1.4, ethylamine 1.6, glycol, 1.7, etc.

For organic solids[1] a similar relation was found to hold, D in this case representing the density and T the absolute melting-point. The value of the constant for solids was found to be 50. A large number of solids were studied, and in general the degree of polymerization in the solid state was found to be double what it was in the liquid. This would not follow, however, from the value of the constants in the two cases, because one depends upon the boiling-points and the other the melting-points.

Küster's work on the determination of the molecular weights of solids in isomorphous mixtures, is the most important work with which comparisons can be made in this field, and it is interesting to note that his results agree with those of Longinescu. For the most part the results of Longinescu with solids will have to be accepted on their face-value until confirmation is obtained.

In the application of the equation to inorganic liquids and solids[2] a difficulty was encountered in the large atomic weights of some of the elements. The weight of the molecules has an effect which the author is unable to explain, but he hopes to be able to clear up this point in a future paper. At present he limits his compounds to those made up of elements having atomic weights less than 40. For these the constants were found to be the same as for organic liquids and solids.

The agreement between his results and those of other workers is very close. Thus, liquid hydrofluoric acid was found by both Vernon and Longinescu to be four times polymerized, while they both found that there are 12 atoms in the molecule of liquid sulphur. The oxides of chlorine and nitrogen were found to be normal by Vernon, Ramsay, and Longinescu. For water the equation gave 5, while Vernon found 4.5 and Ramsay and Shields 3.5. A striking exception is

[1] J. Chim. Phys., Oct., 1903.
[2] *Ibid.*, Nov., 1903.

noted with liquid hydrocyanic acid, which Longinescu found to be six times polymerized, while from previous work it was only supposed to be four. The new number explains much better some of the properties of the compound than the old.

For inorganic solids[1] the results differ greatly, and we have no method of comparison. Most of the solids are found to be highly polymerized. Thus, hydrofluoric acid in the solid state is seven times polymerized, water 9.6, hydrocyanic acid 17.3, ammonia 10, potassium nitrate 6.8, sodium nitrate 5.2, potassium carbonate 20.1, sodium carbonate 19 8, and so on for a long list of substances.

L. S. TAYLOR.

REVIEWS.

A HISTORY OF HINDU CHEMISTRY, from the Earliest Times to the Middle of the Sixteenth Century, A. D., with Sanskrit Texts, Variants, Translation, and Illustrations. By PRAPHULLA CHANDRA RAY, D.Sc., Professor of Chemistry, Presidency College, Calcutta. Vol. I. London: Williams & Norgate.

To quote from the author's preface: "The progress of chemical knowledge among the ancient nations has always had a fascination for me. * * * It was at this stage that I was brought into communication with M. Berthelot some five years ago, a circumstance which has proved to be a turning-point, if I may say so, in my career as a student of the history of chemistry. * * * But I soon found that the task was one of great magnitude. * * * In the present volume only one or two representative works of the Tantric and Iatro-chemical periods have been noticed at length."

This important work is written by an author well fitted for his task and it is hoped that the promised succeeding volumes will soon appear. Certain conclusions of value to the chemical historian should be noticed. Since Berthelot showed that true alchemy began in Egypt about the beginning of our era, the only doubt which overshadowed that conclusion was whether the origin of the Egyptian art might not at some time be found in India. This doubt seems now dispelled. The author finds no definite mention of mercury or bronzing methods before the eighth or possibly even the eleventh century. In fact, early Indian alchemy, developed in the eleventh century (by Chakrapani, 1060, and in the Rasanava) had to do not with metals, but with medicine, and is thus to be sharply distinguished from true Egyptian alchemy, though it may have been derived from it. The Iatro- or medical

[1] J. Chim. Phys., Nov., 1903.

chemistry developed in India was transmitted directly by the Arabians into Western Europe. The author's illustrations are largely drawn from Rasaratna-samuchchaya ("alchemistic collection") of the fourteenth century, the contemporaries of which were such alchemists as Roger Bacon, "Albertus Magnus" "Raymundus Lullus," and Arnaldus, and it appears quite evident that medical alchemy was much more highly developed at that time in India, which was its source, than in Europe.

The famous poison passage of Pliny is quoted as though it originated in India in the Charaka, fifth century B. C., although the only intelligible interpretation of this passage[1] seems to be an alchemistic one and there was no alchemy in India at that time.

To the historian the so-called European alchemy (from the fourteenth to the sixteenth centuries) will now appear pictured as the fusion of two streams. Egyptian alchemy, which taught the identification of the metals by their colors and the transmutation of the metals by their bronzes, was as an art destroyed by Roman edict in the third century. Out of this disaster some of the manuscripts of alchemy were saved by the Syrians and Arabians. But it was not until the medicine which they had just received from India became their principal interest that the Arabians transmitted into Europe both medicine from India and alchemistic writings from Egypt. Here medicine, transplanted from its source, failed to reach the standard attained in India; and alchemy, utterly misunderstood, was translated into medical terms. The philosopher's stone became the elixir of life. So, though the spirit of alchemy had died in Egypt, the hollow terms were used and devoutly believed and alchemy became a drag upon medicine. It was not until the sixteenth century that Iatro-chemistry in Europe was able to make its first advance, when Paracelsus, discarding the empty shell of "alchemy," routed the charlatan and proclaimed that the "object of chemistry is not to make gold but to prepare medicines."

But one question remains to be asked. Why in India did the early promise of progress in the fourteenth century come to naught? Perhaps Professor Ray will tell us this in the succeeding volumes. A. J. H.

DIE ELEKTROMETALLURGIE DER ALKALIMETALLE. Von H. BECKER, Herausgeber von "L'Industrie Elektrochimique," Paris. Monographien über angewandte Elektrochemie, IX Band. Halle, a. S.: Verlag von Wilhelm Knapp. 1903. pp. 135. Price, 6 marks.

As the title implies, there is discussed here the various

[1] Chem. News, 1902, p. 49.

methods for obtaining the alkali metals. A brief account of the chemical methods is followed by an elaborate discussion of the electrochemical. The monograph concludes with a short chapter on electrothermal procedure in obtaining the alkalies and alkaline carbides. H. C. J.

WILHELM OSTWALD. By PAUL WALDEN. Mit zwei Heliogravüren und einer Bibliographie. Leipzig: Verlag von Wilhelm Engelmann. pp. 120. 1904.

This life of Ostwald will be read with interest by all who have had the good fortune to know him, and will be especially welcomed by those who have been privileged to work with him. The life of this remarkable man is largely a history of the development of modern physical chemistry. As is well known, he was the organizer of the "Leipzig School" of Physical Chemists, the founder of their official organ—*The Zeitschrift für physikalische Chemie*—and the investigator who furnished the experimental proof of several of the generalizations upon which the "new chemistry" rests.

The author discusses the life of Ostwald in five periods. The first period (1853 to 1871) includes the boyhood and early school days of Ostwald. The second (1872 to 1875) deals with Ostwald, the student at Dorpat. The third (1875 to 1881) with him as teacher in Dorpat. The fourth (1881 to 1887) period tells us of Ostwald the professor in Riga, and the fifth is the Leipzig period.

As Walden points out, much work was done during the Riga period, but the greatest activity was shown after settling down in Leipzig. Here Ostwald was in the very center of scientific activity, and his genius received unlimited stimulus from his surroundings. Further, he saw a new day for chemical science, to be inaugurated largely through his own efforts. Van 't Hoff had pointed out the fundamental relations between solutions and gases, and Arrhenius had proposed the Theory of Electrolytic Dissociation. Ostwald saw the consequences of these generalizations, probably, as no one else had done, and began to apply them in all directions in physics and chemistry. Under his guidance Nernst made use of them in solving the problem of the primary cell.

A large number of students began to migrate to Leipzig, and with their aid Ostwald worked out experimentally the suggestions that had come to him.

Most of the striking characteristics of Ostwald have been faithfully portrayed by Walden. Perhaps one or two additional points may be referred to. Ostwald always impressed the writer of this review as having a control of physical and

chemical literature that was simply wonderful—matters which other men of far maturer years knew where to find, Ostwald had always at his finger's end. This seemed to apply to almost every phase of Physics, Inorganic Chemistry, and Physical Chemistry.

A personal characteristic which made a lasting impression on us all was the absolute lack of selfishness in our teacher. Investigation after investigation was suggested to us, and when complete we were told to publish it as if it were of our own thinking. This characteristic was so pronounced as to call for special comment.

May the life of Ostwald just written by Walden be but the preface to the longer life of scientific activity which yet remains to him. H. C. J.

MONOGRAPHIEN ÜBER ANGEWANDTE CHEMIE, VII. CYANID-PROZESSE ZUR GOLDGEWINNUNG. Nach einschlägigen Quellen bearbeitet von MANUEL VON USLAR, dipl. Hütteningenieur, unter Mitwirkung von DR. GEORGE ERLWEIN, Vorstand der elektrochemischen Abteilung der Siemens und Halske A. G., Berlin. Mit 30 Figuren und 13 Tabellen im Text und 3 Tafeln. Halle a. S.: Verlag von Wilhelm Knapp. 1903.

In this book of 100 pages and four chapters, besides the introduction, is given much of interest concerning the cyanide process of obtaining gold. The first chapter gives an account of the McArthur Forest and the Siemens-Halske processes. The next describes the methods in actual use in seven works, including the dimensions of the tanks, the amount of cyanide used, the charge per tank, etc. The relative cost is also stated. The fourth chapter, about one-half of the book, is devoted to the modifications of the process. Of most interest to the chemist who is not a specialist in this line is the third chapter, which discusses the chemistry of the process. When gold dissolves in a solution of potassium cyanide two reactions take place:

$$(1)\ 2Au + 4KCN + 2H_2O + O_2 = 2KAu(CN)_2 + 2KOH + H_2O_2;$$

$$(2)\ 2Au + 4KCN + H_2O_2 = 2KAu(CN)_2 + 2KOH.$$

The metal must be in a finely divided state, and even then it will not dissolve if the oxygen of the air is excluded. Upon the latter fact are based a number of patents that are chiefly of scientific interest and of little practical importance. The influence of other constituents of the ore are taken up also. The elements, antimony, arsenic, and tellurium are up to the present "Schmerzenskinder" for those engaged in the

cyanide process, for no cheap and practicable way of dealing with them has been devised. Zinc blende and lead compounds exert an unfavorable influence, as do also iron sulphate and other salts formed by weathering. Carbon dioxide from the air sets hydrocyanic acid free, and even the oxygen may do harm, although it is necessary, as shown above. An excess of it acts in this way:

(1) $KCN + O = KCNO$;

(2) $2KCNO + 3O = K_2CO_3 + CO_2 + N_2$;

(3) $2KCN + CO_2 + H_2O = K_2CO_3 + 2HCN$.

When the gold is in solution it is precipitated by adding metallic zinc. According to the equation,

$$2KAu(CN)_2 + Zn = 2Au + Zn(CN)_2(KCN)_2,$$

1 gram of zinc should precipitate about 6 grams of gold, but here again, on account of side reactions, 40 grams are needed to throw down 6 grams of gold. The chapter includes an account of the analytical methods used at the different works.

C. E. W.

DIRECTIONS FOR LABORATORY WORK IN PHYSIOLOGICAL CHEMISTRY. By HOLMES C. JACKSON, PH.D., Assistant Professor of Physiological Chemistry in the University and Bellevue Hospital Medical College. Second edition. New York: John Wiley & Sons. 1903. pp. 148.

The author has added much new material in this edition. The experiments, which are clearly described, are not fully explained so that the student has to make out the meaning of the experiments for himself. The book is not unique in any particular but conforms to the usual type of manuals on laboratory practice in physiological chemistry. A. S. L.

CONTENTS.

PAGE.

A NEW ELECTRIC FURNACE AND VARIOUS OTHER ELECTRIC HEATING APPLIANCES FOR LABORATORY USE. By H. N. Morse and J. C. W. Frazer 93

CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO:

On Phenylmalonic Nitrile. By John C. Hessler . . . 119

CONTRIBUTIONS FROM THE SHEFFIELD LABORATORY OF YALE UNIVERSITY:

CXV.—*Researches on Pyrimidines. Synthesis of 2-Amino-5-methyl-6-oxypyrimidine.* By Treat B. Johnson and Samuel H. Clapp 130

CONTRIBUTIONS FROM THE NEW YORK AGRICULTURAL EXPERIMENT STATION:

VIII.—*Chemical Changes in the Souring of Milk.* By Lucius L. Van Slyke and Edwin B. Hart 145

IX.—*A Study of the Artificial Digestion of Some Compounds of Casein and Paracasein Contained in Cottage and Cheddar Cheese.* By Lucius L. Van Slyke and Edwin B. Hart 154

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF LEHIGH UNIVERSITY:

VI.—*Propanetrisulphonic Acid.* By William B. Schober . 165

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE:

On Certain Derivatives of Trichlortrinitrobenzol. By C. Loring Jackson and Paul Shortt Smith 168

REVIEWS.

Quantitative Chemical Analysis 181

The Phase Rule and Its Applications 183

A Laboratory Manual of Physiological and Pathological Chemistry for Students in Medicine 184

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American Chemical Journal.

This Journal contains original articles by American chemists; reviews of works relating to chemistry; reports on progress in the various departments of chemistry; and items of general interest to chemists. Twelve numbers of about 100 pages each are published annually, at regular intervals, and form two volumes. A number is issued each month. The subscription price is $5.00 a year in advance; single numbers 50 cents.

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